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UNIVERSITY OF ALBERTA

SYNTHESIS AND REACTIVITY OF BIS(DIPHENYLPHOSPHINO)METHANE-BRIDGED DIRUTHENIUM COMPLEXES

by

PAUL MARK LYNE SANDERCOCK

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A THESIS

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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1990

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled SYNTHESIS AND REACTIVITY OF BIS(DIPHENYLPHOSPHINO)METHANE DIRUTHENIUM COMPLEXES submitted by PAUL MARK LYNE SANDERCOCK in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

J. Takats (Supervisor)

M. Cowie

R. E. D. McClung

S. Wanke

Date: June 6, 1990

To my family

Abstract

The preparation and reactivity of bis(diphenylphosphino)methane-bridged diruthenium complexes have been investigated.

Preparation of the starting material, $Ru_2(CO)_7(\mu\text{-dppm})$, **2**, by either the photochemical reaction of the two mononuclear species $Ru(CO)_4(\eta^1\text{-dppm})$, **1**, and $Ru(CO)_5$, or the photofragmentation of $Ru_3(CO)_{10}(\mu\text{-dppm})$, is described. Complex **2** undergoes a very facile displacement of CO in the presence of diazomethane to give $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$, **10**. Reaction of **2** with ethyne gives the diruthenacyclopentenone species, $Ru_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$, **9**, via the insertion of a CO ligand into the metal-alkyne bond. In contrast to the latter reaction, the reaction of **2** with the activated alkynes dimethylacetylene dicarboxylate (dmad) and diphenylacetylene gives the 1,2-diruthenacyclobutene complexes $Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CO_2CH_3)_2](\mu\text{-dppm})$, **12**, and $Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(C_6H_5)_2](\mu\text{-dppm})$, **13**, respectively. Spectroscopic characterization of **12** and **13** in solution indicate that the dmad ligand of **12** is situated perpendicular to the "$Ru_2(\mu\text{-dppm})$" core, while the diphenylacetylene ligand of **13** is oriented *trans* to the bridging dppm ligand of the "$Ru_2(\mu\text{-dppm})$" core. Attempts to insert more ethyne units into **9** via a photochemical route are also described.

Complex **2** reacts readily with dihydrogen to give the dihydride, $Ru_2(CO)_6(H)_2(\mu\text{-dppm})$, **8**, which reversibly adds CO to quantitatively regenerate the starting material. The extreme lability of dihydrogen from **8** prevents its isolation. Characterization of **8** in solution was accomplished by extensive, multinuclear n.m.r. experiments which also revealed that **8** exists as a mixture of isomers, **8a** and **8b**, in a 2:1 ratio. Complex **8** reacts with ethyne and diazomethane to give **9** and **10** respectively, compounds already seen from the reaction of **2** with these reagents. Complex **8** also reacts smoothly with ethylene to give $Ru_2(CO)_4[\mu\text{-}$

$O{=}C(C_2H_5)]_2(\mu\text{-dppm})$, **11**, a compound containing two bridging propionyl groups arranged in a geminal fashion. Plausible pathways for the formation of the dihydride **8** from **2**, and for the reaction of **8** with ethylene to give **11** are proposed.

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List of Abbreviations

Å	angström
br	broad
CHT	cycloheptatriene (C_7H_8)
COD	cyclooctadiene (C_8H_{12})
Cp	cyclopentadienyl (C_5H_5)
Cp*	pentamethylcyclopentadienyl (C_5Me_5)
δ	chemical shift (versus TMS)
d	doublet
dd	doublet of doublets
dmad	dimethylacetylene dicarboxylate [$C_2(CO_2CH_3)_2$]
dmpm	bis(dimethylphosphino)methane ($Me_2PCH_2PMe_2$)
dppe	bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$)
dppee	bis(diphenylphosphino)ethylene [$Ph_2PC(CH_2)PPh_2$]
dppm	bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$)
dt	doublet of triplets
Et	ethyl
GC	gas chromatography
Hz	hertz
IR	infrared
J	coupling constant
K	kelvin
λ	wavelength
m	medium
ms	millisecond
Me	methyl

MHz	megahertz
MS	mass spectrometry
n.m.r.	nuclear magnetic resonance
ν	stretching frequency
Ph	phenyl
p.p.m.	part per million
s	strong (IR); singlet (n.m.r.)
sh	shoulder
t	triplet
THF	tetrahydrofuran (C_4H_8O)
TMS	tetramethylsilane (Me_4Si)
U.H.P.	ultrahigh purity
u.v.	ultraviolet
v	very
w	weak

Chapter One

Introduction

1.1. Heterogeneous and Homogeneous Catalysis

Catalysts have an important role in many industrial-scale processes. During the first decade of this century Haber, Bosch, and Mittasch laboured to find a catalyst that could be used to generate ammonia from dinitrogen.[1] An iron catalyst operating at 670 K under 150-350 atmospheres of dinitrogen and dihydrogen was eventually developed and commercial production of synthetic ammonia by the "Haber Process" began in Germany in 1913-14.[2] Another example of industrially important catalysts are the Ziegler-Natta polymerization catalysts, discovered in the early 1950's. The most common Ziegler-Natta catalyst consists of $TiCl_4$ activated by trialkylaluminum, and is used in the synthesis of such polymers as polyproplyene.[3] Refinement of already well established catalysts such as the two examples cited above and the search for more specific, more active catalysts continues to fuel catalytic research and the search for models of such processes.

A catalyst can be classified as belonging to one of two distinct categories;[4] a catalyst can be either heterogeneous or homogeneous. Heterogeneous catalysts are separated from the reactants by a phase boundary. Homogeneous catalysts are of the same phase as the reactants and no phase boundary exists. Aspects of these two catalytic types will be described briefly.

Heterogeneous catalysts are often comprised of transition metals, or their compounds, bound to a solid support, over which reactants are passed. Like the Haber Process, these reactions often require forcing conditions. However, the ease of separation of product from the catalyst is of great practical advantage.

Greater selectivity and milder reaction conditions are the hallmark of homogeneous catalysts. Unfortunately the separation of product from reactants and the catalyst is often difficult because they are in the same phase. Homogeneous catalysts in solution are well suited to mechanistic studies as the formation of intermediates and products can be monitored and characterized by such accessible techniques as infrared (IR) and ^1H n.m.r. spectroscopy.

Some attention has been given towards a direct comparison of the behaviour exhibited by both types of catalysts.[5] Attempts to meld the selectivity and relatively mild reaction conditions characteristic of a homogeneous catalyst with the ease of product separation found with heterogeneous catalysts have been made by placing a homogeneous catalyst on an inert support.[6] Despite such work our knowledge of catalysis and catalysts is often limited.

1.2. Some Aspects of Fischer-Tropsch Catalysis

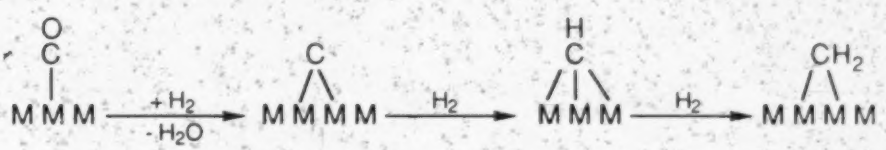
Transition metal clusters have received a great deal of attention in recent years not only for their potential to act as homogeneous catalysts,[7,8] but also for the insight they provide into heterogeneous catalysis.[8] Study of the coordination of small molecules, such as dihydrogen or unsaturated organic substrates to polynuclear metal centres, may provide useful information about the behaviour of these molecules on a metal surface.[8,9] The elucidation of probable intermediates for the well known Fischer-Tropsch synthesis (1),

$$nCO + 2nH_2 \rightleftharpoons -(CH_2)_n- + nH_2O \qquad (1)$$

from the reactions of transition metal cluster complexes demonstrates the power of organometallic complexes to model surface reactions.[9,10]

Fischer and Tropsch had originally proposed that hydrogenation of CO led to formation of methylene groups which would then polymerize to form hydrocarbon chains.[9] The mechanism for methylene formation is thought to occur via dissociative chemisorption of CO, resulting in a bridging carbide followed by stepwise hydrogenation to give μ-CH, μ-CH_2, and μ-CH_3 groups.[12] Evidence supporting CO dissociation prior to attack by hydrogen has been reviewed recently by Bilone and Sachtler,[13a] and will not be further developed here. The recent synthesis of dinuclear iron complexes containing μ-CH, μ-CH_2, and μ-CH_3 ligands serves as a useful model in support of the "carbide/methylene" mechanism[13b] (Scheme 1.1).

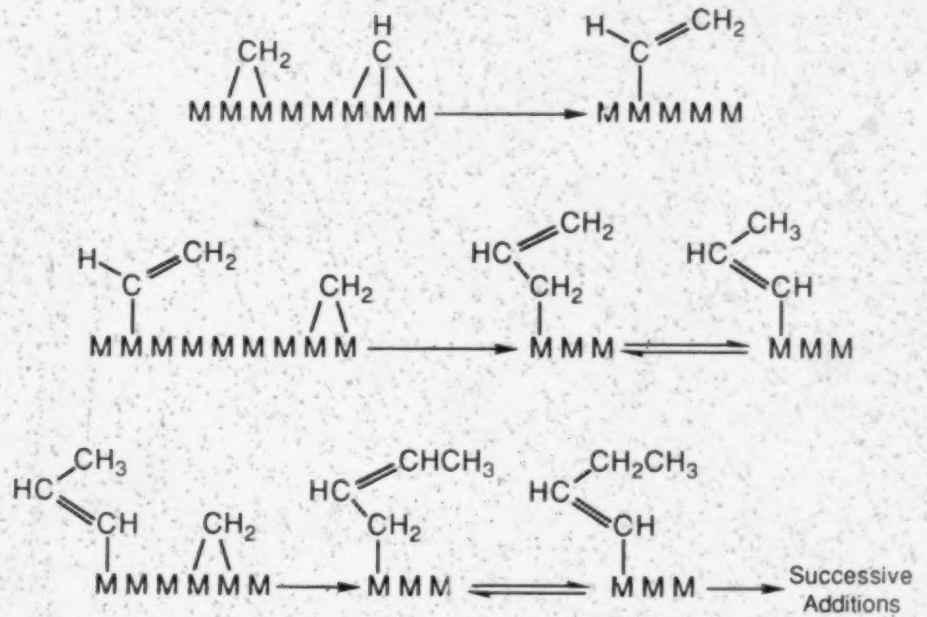
Scheme 1.1: Carbide/Methylene Mechanism



The polymerization of methylene groups to form hydrocarbons has been investigated by Brady and Pettit.[13c] Comparisons were made between the hydrocarbon reaction products resulting from the reaction of synthesis gas (CO/H_2) and the reaction of diazomethane/H_2 mixtures over various metals such as Fe, Co, and Ru, (diazomethane is a reagent commonly used to form μ-CH_2 groups on coordinatively unsaturated transition metal complexes[13d]). They found both reactions yielded very similar compositions of products and concluded from this that a common mechanism for the two processes may be occurring. Although the simple "carbide/methylene" mechanism does have strong support, the formation of olefins and branched hydrocarbons, observed in addition to the expected production of alkanes, needs to be explained as well. It has long been understood

that during the chain termination step metal-alkyl β-hydride elimination will give α-alkenes. Very recently Maitlis has explained the formation of β-alkenes and branched hydrocarbons by proposing a modification to the "carbide/methylene" mechanism.[13e] The proposal states that reduction of CO, to generate bridging methyne and methylene units, can lead to formation of σ-bound vinyls. This process has been successfully modelled on a dirhodium complex by Maitlis.[13e] Successive additions of methylene groups, and subsequent rearrangements, leads to chain propagation (Scheme 1.2).

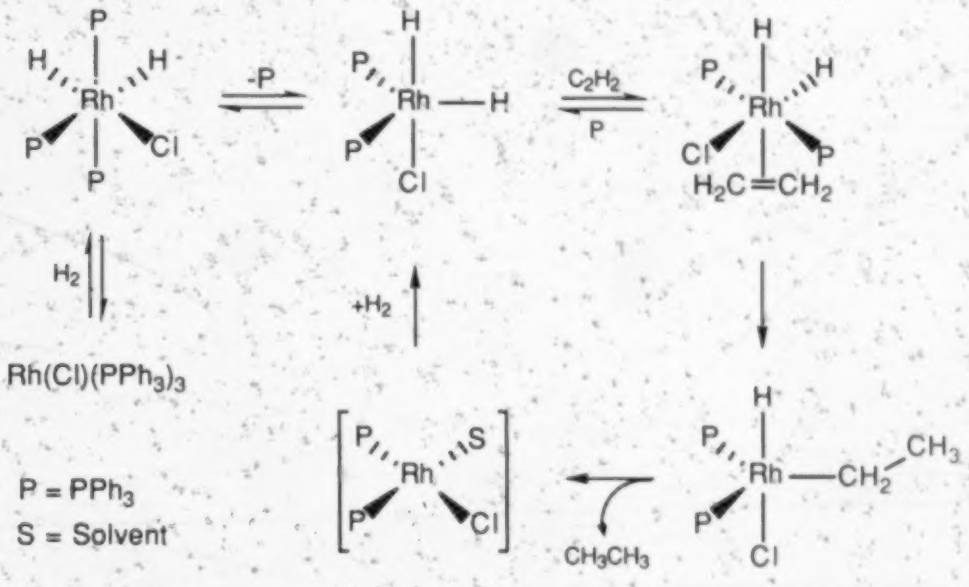
Scheme 1.2: Proposed Mechansim for Carbon Chain Propagation on a Metal Surface



1.3. Hydrogenation Catalysts and Catalytic Models

Early work by Wilkinson with $Rh(Cl)(PPh_3)_3$[14] demonstrated that homogeneous catalytic hydrogenation of alkenes could be achieved. The process proceeds via oxidative addition of dihydrogen, followed by ligand loss to generate a coordinatively unsaturated species that can then bind an alkene. Transfer of a hydride to the alkene and reductive elimination of the alkane followed by uptake of another molecule of dihydrogen completes the cycle (Scheme 1.3). A more

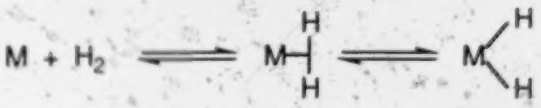
Scheme 1.3: Mechanism for Hydrogenation of Alkenes by Wilkinson's Catalyst



complicated but more realistic scheme would consider the possibility of solvent coordination to the unsaturated species formed during the reaction.[15]

Modeling the binding and activation of dihydrogen with transition metal complexes is of fundamental importance to the development and "tailoring" of

homogeneous and heterogeneous catalysts.[16] Until recently only classical, covalently bound hydrides were considered to exist. Non-classical, η^2-dihydrogen complexes were thought to exist only as a short-lived intermediates during the formation of classical dihydrides.



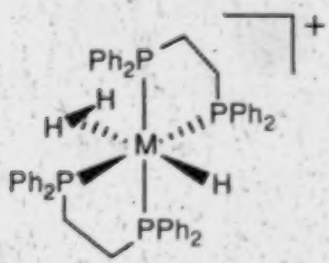
However, in 1984 Kubas[17] showed unequivocally, by neutron diffraction studies, that the side-on bonded dihydrogen ligand did exist. Later, η^2-dihydrogen ligands were more conveniently identified in solution by using relaxation techniques in ^1H n.m.r. spectroscopy.[18] Typical relaxation times for η^2-dihydrogen ligands are short (T_1 ca. 4-100 ms). The short times are thought to be a result of the relatively short distance between hydrogens allowing one to rapidly relax the other. Classical hydrides have relaxation times that are considerably longer (T_1 > 350 ms).

The bonding mode of the η^2-dihydrogen ligand can be described as a two part synergic interaction, analogous to the well known synergic interaction between a transition metal and the π-acid ligand CO. The first part is the donation of electron density to a vacant metal p-orbital from the bonding σ-orbital of H_2. The second part is a backbonding interaction in which electron density is donated from a filled metal d-orbital to the antibonding σ*-orbital of H_2.[16a] The degree of back-

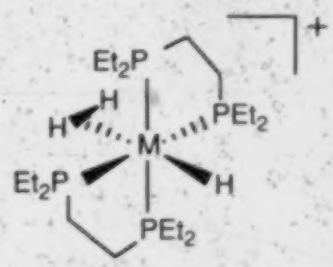
bonding, which is a function of the electron density on the metal, is thought to be mostly responsible for the retention or disruption of the H-H bond.[16b] The electron

donor ability is dependent both on the position of the metal in the periodic table and on the ligand environment of the complex.

Morris has shown that within the Fe, Ru, Os triad a hydride and an η^2-dihydrogen ligand can be present in the same complex,[19] $[M(\eta^2\text{-}H_2)(H)(R_2PCH_2CH_2PR_2)_2]^+$, where M = Fe, Ru for R = Ph, and M = Fe, Ru, Os for R = Et. In the ^1H n.m.r. spectra of the complexes an intramolecular exchange of the terminal hydride with the hydrogens of the dihydrogen ligand is observed. The barriers to the intramolecular exchange were estimated from the susceptibility of exchange of H_2 with D_2, from the T_1 values measured for the hydride and dihydrogen ligand, and from the coupling constants $^2J_{(P\text{-}H_2)}$. It was found that the



M = Fe, Ru

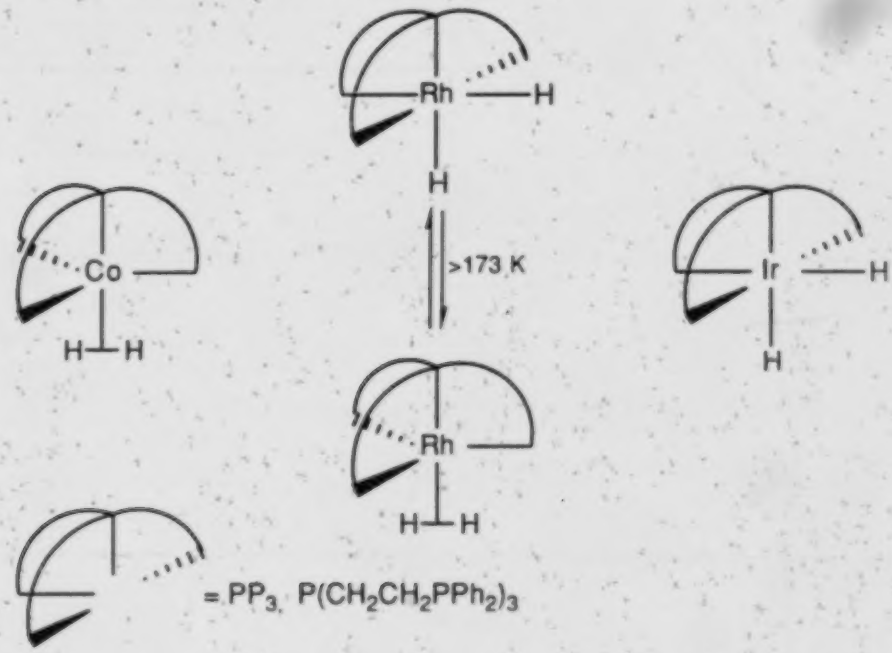


M = Fe, Ru, Os

H-H interactions decrease in the order Ru > Fe > Os within the triad, and for a given metal a stronger H-H interaction was observed for the less basic diphosphine ligand (R = Ph).[19b]

However, Bianchini and co-workers have shown that by descending the Co, Rh, Ir triad, addition of H_2 to the $M(PP_3)^+$ complexes results in the formation of compounds containing either an η^2-dihydrogen ligand, or classical *cis*-dihydride ligands.[20] In the Co case there is not enough back donation from the metal d-orbitals into the antibonding σ^*-orbitals of the dihydrogen ligand to result in H-H bond cleavage. Whereas in the Rh (below 173 K) and the Ir complexes there is

sufficient M to $H_2(\sigma^*)$ interaction to activate and cleave the H-H bond and cause formation of the *cis*-dihydride.



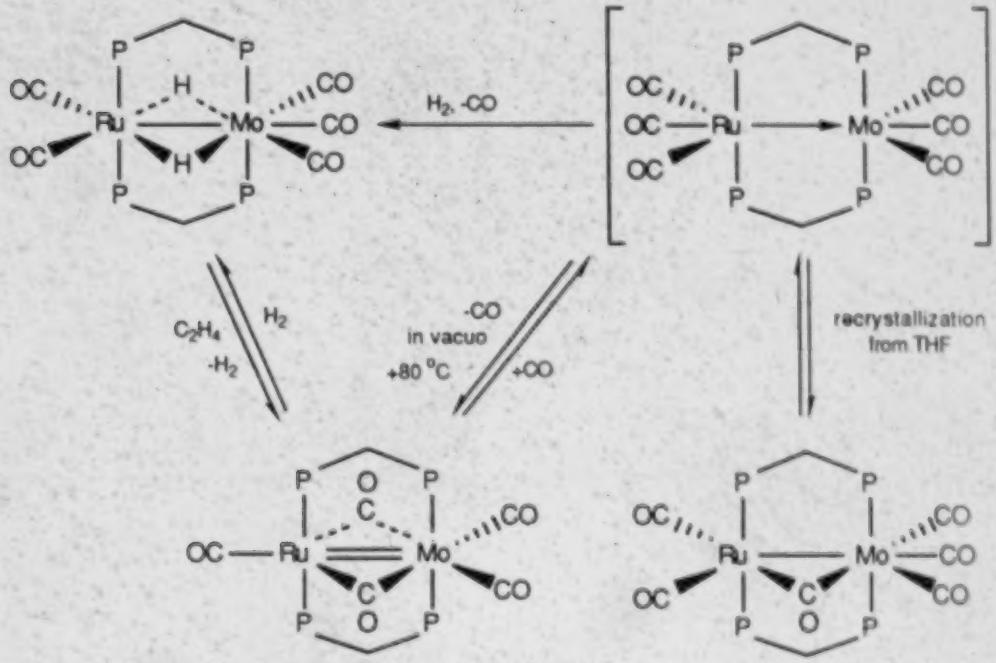
A heterobimetallic "RuMo" complex, $MoRu(CO)_6(\mu\text{-dppm})_2$, has been shown to reversibly bind dihydrogen in solution to give the dihydrido-bridged complex $MoRu(\mu\text{-}H)_2(CO)_5(\mu\text{-dppm})_2$[21] (Scheme 1.4).

1.4. Stabilization of Bimetallic Complexes Using Diphosphine Ligands

As shown in the examples above, phosphine ligands have a well established role in organometallic chemistry.[22] These ligands are recognized for their ability to impart two properties considered desirable for an effective catalyst. First phosphines bind strongly with low oxidation state transition metals to give stable M-P bonds,[23] second they tend to provide good solubility in organic solvents, an important consideration in homogeneous catalysis. However, most of the examples

cited above are mononuclear transition metal complexes, which may not be suitable as models for a chemical transformation occurring on a metal surface.

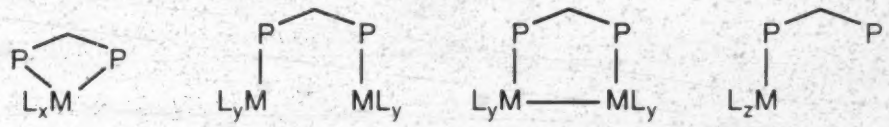
Scheme 1.4: Reversible Bonding of Dihydrogen to $MoRu(CO)_6(\mu\text{-dppm})_2$

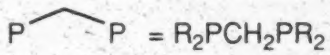


It is thought that enhanced catalytic activity may result from cooperative interactions between two or three adjacent transition metal centres.[24] A dinuclear transition metal complex is the simplest model available to test this idea; however, under typical catalytic reaction conditions cleavage of the metal-metal bond may result causing disruption of the model.[25] Therefore, an effective di- or polynuclear catalytic model (or catalyst) must be resistant to metal-metal bond scission while maintaining a high degree of reactivity.

The use of diphosphine ligands to stabilize dinuclear transition metal complexes has been developed extensively.[26] Ligands of the general form $R_2P(CH_2)_nPR_2$ have been utilized and a wide variety of derivatives are known. Varying the alkyl substituent on phosphorous can give variations in electronic and

steric effects,[22] while variations of the backbone chain length (n = 1 to 4) will alter the preference of the ligand to either chelate or bridge. In the series $[RhCl(CO)(Ph_2P(CH_2)_nPPh_2)]_m$[27] it was found that when n = 2 chelation is favoured (m = 1), and when n = 1, 3, or 4 a bridging mode was adopted (m = 2). A ligand of the type $R_2PCH_2PR_2$ would form a particularily strained four-membered ring if it were to chelate, and so it shows a much greater tendency to





act either as a monodentate moiety to one metal centre, or as a bidentate unit bridging two metal centres. It is ligands of this latter type that are of interest in the synthesis of bimetallic complexes.

Two well known diphosphine ligands capable of bridging two metal centres are bis(diphenylphosphino)methane, dppm, and bis(dimethylphosphino)methane, dmpm. The chemistry of dppm has been studied extensively and is the subject of a review in 1983 by Puddephatt.[26a] More recently Chaudret and co-workers have reviewed the use of dppm in dinuclear complexes.[28] Dmpm has received far less attention most likely because the ligand is air sensitive and difficult to prepare.[29] This simple ligand is of interest because the methyl groups render it much more basic and much less demanding sterically than dppm.[30]

As evidenced by Puddephatt's review much work has been done on complexes containing the "$M_2(\mu\text{-dppm})_2$" skeleton. Complexes such as $[Rh_2(CO)_3(\mu\text{-dppm})_2]^+$,[31] $[Pd_2Cl_2(\mu\text{-dppm})_2]$[32], and more recently,

$[Ir_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^{+}$[33a] and $[Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$[33b] have shown a remarkable ability to activate small molecules. The dipalladium complex is known to insert small molecules such as carbon monoxide[32b] and activated alkynes[32c] into the metal-metal bond, a behaviour that has also been observed in some diiridium complexes.[32d] More recent investigations of small molecule activation have dealt with the addition of dihydrogen to diiridium complexes. $[Ir_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][BF_4]$ reacts readily with an excess of H_2 to give the tetrahydride species $[Ir_2(H)_4(\mu\text{-}Cl)(CO)_2(\mu\text{-}dppm)_2][BF_4]$.[33a] Refluxing a solution of this complex causes H_2 loss and formation of the well characterized dihydride, $[Ir_2(H)_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}dppm)_2][BF_4]$.[33a] Further investigation showed that the tetrahydride species is present in solution in two isomeric forms, and structures for both isomers have recently been reported.[33c] A similar reaction of the sulfur bridged complex $[Ir_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2]$ with H_2 results in oxidative addition of one equivalent of H_2 to give the dihydride complex $[Ir_2(\mu\text{-}S)(H)_2(CO)_2(\mu\text{-}dppm)_2]$.[33b] It would be of interest to develop the chemistry of the sterically less crowded singly-bridging complexes with an "$M_2(\mu\text{-}R_2PCH_2PR_2)$" skeleton (R = Ph, or Me) because one would expect such complexes to be more open to coordination by substrates.

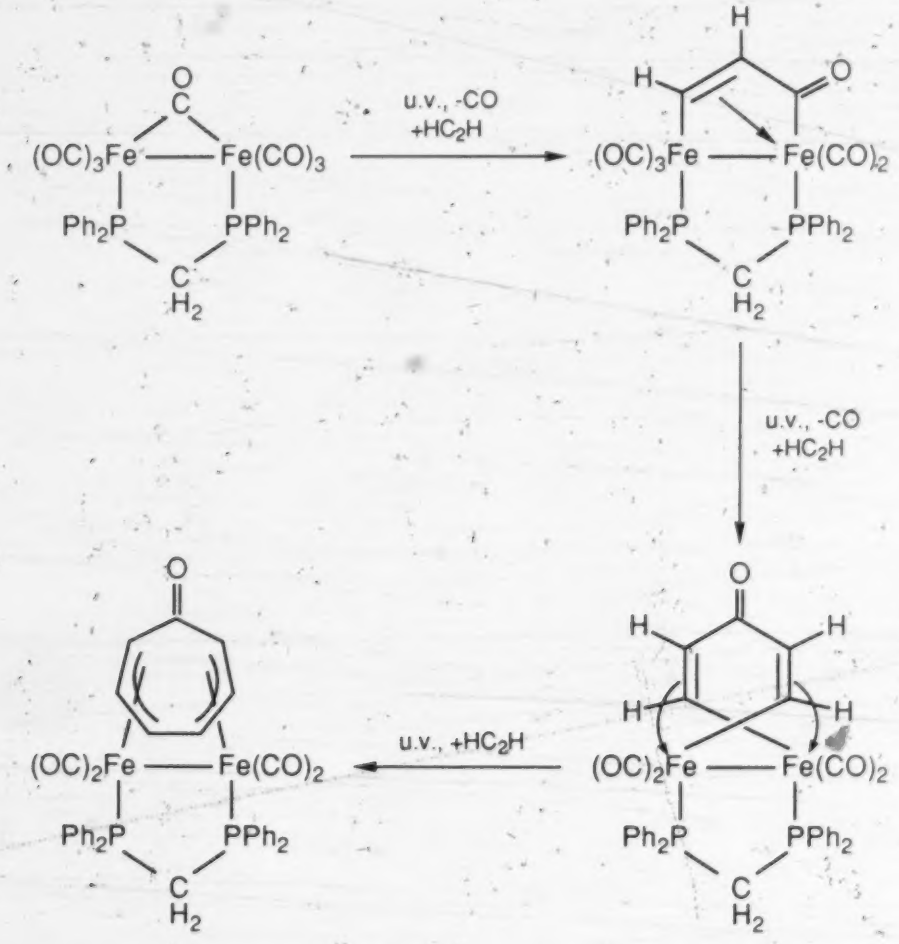
1.5. Chemistry of Phosphine-Bridged Complexes of Iron and Ruthenium

The iron carbonyl complex, $Fe_2(CO)_7(\mu\text{-}dppm)$, has been prepared by the substitution of dppm into $Fe_2(CO)_9$,[34] and has been shown to undergo successive insertions of ethyne under photochemical conditions to form a diiron tropone complex[35] (Scheme 1.5). The analogous $Fe_2(CO)_7(\mu\text{-}dmpm)$ complex has been made,[30] however, no attempts to study its reactivity have been reported.

An improved synthesis for $Fe_2(CO)_7(\mu\text{-dppm})$ has been achieved by reacting $Fe(CO)_4(\eta^1\text{-dppm})$ with the "$Fe(CO)_4$" transfer reagent, $Fe(CO)_4(THF)$, under u.v. irradiation.[36] The monodentate phosphine, $Fe(CO)_4(\eta^1\text{-dppm})$ has also been used as a starting point toward the systematic preparation of heterobimetallic complexes.[37]

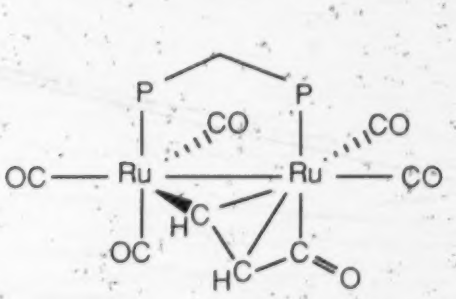
The analogous ruthenium carbonyl complexes are expected to show an even greater reactivity.[38] However, Chaudret has noted in his review of dinuclear complexes of dppm that there is a surprising lack of diruthenium complexes

Scheme 1.5: Stepwise Insertion of Ethyne on a Diiron Centre

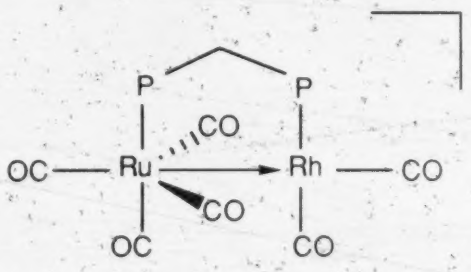


containing dppm ligands. He has attributed this deficiency to the difficulty in obtaining dinuclear starting materials.

Very recently our research group reported the successful synthesis of $Ru(CO)_4(\eta^1$-dppm) and $Ru_2(CO)_7(\mu$-dppm), as well as some preliminary reactivity studies.[39] As with the diiron complex, $Ru_2(CO)_7(\mu$-dppm) was prepared photochemically by reacting $Ru(CO)_4(\eta^1$-dppm) with $Ru(CO)_5$. As expected, the preliminary reactivity studies demonstrated that the diruthenium complex was very reactive in solution. Reaction with ethyne occurred under mild thermal conditions to give the dimetallacyclopentenone, $Ru_2(CO)_5[\mu$-$C_2H_2C(O)](\mu$-dppm), (**a**). Reaction of the monodentate phosphine, $Ru(CO)_4(\eta^1$-dppm), with $[Rh(CO)_2(solv)_2]^+$ gave the heterobimetallic complex, $[(\mu$-dppm)$Ru(CO)_4$-$Rh(CO)_2]^+$, (**b**). Formation of this heterobimetallic complex proved to be problematic as the reaction was very sensitive to experimental conditions, unlike the analogous reaction between $Fe(CO)_4(\eta^1$-dppm) and $[Rh(CO)_2Cl]_2$ which, at room temperature, smoothly gave $(\mu$-dppm)$Fe(CO)_4Rh(CO)Cl$.[40]



(**a**)



(**b**)

The only diruthenium complex of dmpm reported is $Ru_2(CO)_5(\mu$-dmpm)$_2$.[41] Examples of mononuclear dmpm complexes of iron and ruthenium are also known.[29] Preparation of the sterically less encumbered, but potentially more reactive, diruthenium complex, $Ru_2(CO)_7(\mu$-dmpm), has remained elusive.

The objective of this thesis was to extend the study of the reactivity of $Ru_2(CO)_7(\mu\text{-dppm})$ with a variety of substrate molecules. The focus of these studies will be: (a) to investigate the reaction with molecular hydrogen as a first step towards modeling H_2 activation on a diruthenium complex; (b) to investigate the coordination geometry of several different alkynes; and, (c) to investigate the potential of this diruthenium complex to serve as a model for the step-wise insertion of ethyne to form larger metallaheterocycles. Attempts to synthesize the dmpm analogue, $Ru_2(CO)_7(\mu\text{-dmpm})$, in the hope of evaluating the effect of changing the diphophine bridge on reactivity, will also be discussed.

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Chapter Two

Synthesis and Characterization of Bis(diphenylphosphino)methane and bis(dimethylphosphino)methane Derivatives of Ruthenium Carbonyls

2.1. Introduction

Cotton and Troup were the first to prepare the diphosphine-bridged, diiron complex, $Fe_2(CO)_7(\mu\text{-dppm})$.[1] The complex was prepared by the thermal reaction of dppm with $Fe_2(CO)_9$, and an X-ray structure was obtained. At nearly the same time Wegner and co-workers were investigating the possiblity of forming similar diiron complexes via a photochemical route.[2] They found that photolysis of $Fe(CO)_5$ in the presence of dppm gives a mixture of products. Careful separation yielded two dinuclear species, $[Fe(CO)_4]_2(\mu\text{-dppm})$ (25%) and $Fe_2(CO)_7(\mu\text{-dppm})$ (16%), and two mononuclear complexes, $Fe(CO)_3(\eta^2\text{-dppm})$ (11%) and $Fe(CO)_4(\eta^1\text{-dppm})$ (16%). It was postulated by Wegner that the latter complex might be an intermediate[2] in the formation of the two bimetallic derivatives. However, further work to confirm this postulate was not undertaken, most likely a result of the poor synthetic yields of $Fe(CO)_4(\eta^1\text{-dppm})$.

Recently Shaw has shown that $Fe(CO)_4(\eta^1\text{-dppm})$ can be prepared by treating dppm with $Fe_2(CO)_9$ in THF.[3] This procedure has also been successfully employed by Hogarth and Knox,[4] who have demonstrated the general utility of this reaction by treating a diphosphine ligand, L_2, (L_2 = dppm,[4a] dmpm,[4a] or dppee[4b]) with $Fe_2(CO)_9$ in THF to give the species $Fe(CO)_4(\eta^1\text{-}L_2)$. Photolysis of $Fe(CO)_4(\eta^1\text{-}L_2)$ in the presence of $Fe(CO)_5$ affords the dinuclear complex $Fe_2(CO)_7(\mu\text{-}L_2)$.[4a] Finally, Shaw has established that the mononuclear iron complex is a useful building block for the synthesis of heterobimetallic complexes containing a bridging dppm ligand.[5]

From these results $Ru(CO)_4(\eta^1$-dppm), **1**, appeared to be a potential building block from which the dinuclear complex $Ru_2(CO)_7(\mu$-dppm), **2**, may be formed, and prompted this research group to attempt the preparation of **1** and **2**. Similarily, $Ru(CO)_4(\eta^1$-dmpm), **3**, was seen as a possible route to the preparation of the diruthenium complex, $Ru_2(CO)_7(\mu$-dmpm), **4**. To our knowledge the successful synthesis of the analogous iron complex, $Fe(CO)_4(\eta^1$-dmpm), is not known; however, the diiron complex, $Fe_2(CO)_7(\mu$-dmpm), has been prepared by reacting $Fe_2(CO)_9$ with dmpm in diethyl ether at room temperature.[6]

2.2. Synthesis and Characterization of $Ru(CO)_4(\eta^1$-dppm) and $Ru_2(CO)_7(\mu$-dppm)

2.2.1. $Ru(CO)_4(\eta^1$-dppm)

The reaction of dppm with the known "$Ru(CO)_4$" transfer reagents $Ru(CO)_5$,[7a] $Ru(CO)_4(\eta^2$-$C_2H_4)$,[7a] and $Ru(CO)_4(\eta^2$-$CH_2CHCO_2CH_3)$[7b] was very slow, ultimately forming mixtures consisting of **1**, and the known trinuclear complexes $Ru_3(CO)_{12}$, and $Ru_3(CO)_{10}(\mu$-dppm).[8] However, transfer via the much more labile species $Ru(CO)_4(\eta^2$-$CH_2CHCH_3)$[9] led to the successful synthesis of **1** in good yield (70%).

$$Ru(CO)_5 + CH_2CHCH_3 \xrightarrow[\text{pentane, RT}]{h\nu,\ \lambda \geq 370\ nm} Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3)$$

$$Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3) + \text{dppm} \xrightarrow[\text{pentane, 0 °C}]{\text{toluene}} Ru(CO)_4(\eta^1\text{-dppm})$$

1

Since the above synthesis requires the handling of the rather touchy $Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3)$ compound, an alternate route to the synthesis of **1** was sought. We turned our attention to the well known method of labilizing coordinated carbon monoxide by its reaction with trimethylamine-N-oxide[10] to produce the good leaving group CO_2. Indeed, recently Basolo has achieved facile replacement of CO by PPh_3 on $M(CO)_5$ (M = Fe, Ru, Os) in the presence of $(CH_3)_3NO$.[11] These reactions were carried out in 1:2 (v/v) ethanol/n-hexane mixed solvent. The mixed solvent system provided sufficient solubility for $(CH_3)_3NO$, while the hydrocarbon was used to slow the reaction so that it could be monitored by conventional spectroscopy.[11]

Initially the preparation of **1** was attempted by reacting a mixture of $(CH_3)_3NO$ and dppm with $Ru(CO)_5$ in 1:2 (v/v) THF/n-pentane mixed solvent. The reason for using this mixed solvent system was that $Ru(CO)_5$ can be readily generated *in situ* as a hydrocarbon solution, while $(CH_3)_3NO$ and dppm are soluble in THF. However, mixtures of products were obtained. Several other mixed solvent systems were tried. The reaction carried out in 1:2:3 (v/v/v) ethanol/THF/n-pentane mixed solvent gave the highest yield of **1** (Table 2.1). The product is isolated as a yellow-white solid and is stable in the air and under light for short periods of time.

Table 2.1: Mixed Solvent Systems Used to Generate $Ru(CO)_4(\eta^1\text{-dppm})$, **1**

Mixed Solvent (v/v)	Yield $Ru(CO)_4(\eta^1\text{-dppm})$
ethanol/n-pentane (1:2)	17%
ethanol/chloroform/n-pentane (1:2:3)	60%
ethanol/THF/n-pentane (1:2:3)	71%

The spectroscopic characteristics of $Ru(CO)_4(\eta^1$-dppm) are similar to those already reported for the analogous mononuclear iron species, $Fe(CO)_4(\eta^1$-dppm)[2] and $Fe(CO)_4(\eta^1$-dppe).[12] The crystal structure of the closely related $Fe(CO)_4(\eta^1$-dppe)[12] reveals that a trigonal bipyramidal geometry is adopted with the η^1-diphosphine ligand in the axial position. All three compounds exhibit similar carbonyl stretching patterns in their IR spectra and so one might expect them to have similar geometries as well (Table 2.2).

Table 2.2: Infrared Data for $M(CO)_4(\eta^1$-dppm) Complexes (M = Fe, Ru)

Compound	IR ν_{CO} (cm^{-1})
$Ru(CO)_4(\eta^1$-dppm) **1**	2061s, 1989m, 1956s, 1944s [a]
$Fe(CO)_4(\eta^1$-dppm) [c]	2046m, 1980m, 1948s, 1936s [b]
$Fe(CO)_4(\eta^1$-dppe) [c]	2052s, 1980m, 1947s, 1939s [b]

[a] Solvent: pentane
[b] Solvent: cyclohexane
[c] Keiter, R. L.; Rheingold, A. L.; Hamerski, J.; Castle, C. *Organometallics*, **1983**, *2*, 1635.

By considering not only the number of carbonyl bands, but also their relative intensities,[13a,c] an accurate prediction concerning the geometry of the complex and the position of phosphine substitution can often be made. The C_{3v} symmetry of the trigonal bipyramidal $M(CO)_4L$ unit leads to the expectation of three carbonyl stretching bands in the IR spectrum;[14] however, the axially substituted complex, $Fe(CO)_4(\eta^1$-dppe), has four bands (Table 2.2). This is typical for this type of complex[12] because the axial diphosphine ligand lowers the symmetry of the molecule[12] which results in the splitting of the low frequency E band to give rise to

four absorptions.[13b] Although four bands would also be expected for an equatorially substituted complex (C_{2v} symmetry) the relative intensities and positions of the bands would be different.[13b,c]

In the ^1H n.m.r. spectrum of **1** the methylene protons of the dppm ligand appear as a doublets of doublets at δ 3.33 p.p.m. (J_{PH} = 9 Hz, $J_{P'H}$ = 2 Hz). Two signals are observed in the $^{31}P\{^1H\}$ n.m.r. spectrum because the coordinated and uncoordinated phosphorus atoms of the η^1-dppm ligand are chemically inequivalent. The $^{31}P\{^1H\}$ n.m.r. of free dppm consists of a singlet at δ -22.7 p.p.m.. Thus we can assign the uncoordinated phosphorus atom of **1** to the doublet ^{31}P resonance at δ -26.2 p.p.m. ($J_{PP'}$ = 97.6 Hz), and the phosphorus coordinated to ruthenium to the doublet ^{31}P resonance at δ +38.3 p.p.m. ($J_{PP'}$ = 97.6 Hz). The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of $Fe(CO)_4(\eta^1$-dppm) have been reported[2,12] and agree well with the n.m.r. data observed for **1** (Table 2.3).

Table 2.3: ^1H and $^{31}P\{^1H\}$ n.m.r. Data for $M(CO)_4(\eta^1$-dppm) Complexes (M = Fe, Ru)

Compound	N.M.R. data δ (p.p.m.) [a,b]	
	^1H	$^{31}P\{^1H\}$
$Ru(CO)_4(\eta^1$-dppm) **1**	7.40 m (20H) 3.33 dd (2H, J_{PH} = 9.0)	38.3 d (Ru-P, $J_{PP'}$ = 97.6) -26.2 d (Free, $J_{PP'}$ = 97.6)
$Fe(CO)_4(\eta^1$-dppm)	7.22 m (20H) [c] 3.54 dd (2H, J_{PH} = 9)	65.9 d (Fe-P, $J_{PP'}$ = 80) [d] -25.7 d (Free, $J_{PP'}$ = 80)

[a] Coupling constants reported in Hz
[b] Solvent: dichloromethane-d_2
[c] Wegner, P. A.; Evans, L.; Haddock, J. *Inorg. Chem.*, **1975**, *14*, 192.
[d] Keiter, R. L.; Rheingold, A. L.; Hamerski, J.; Castle, C. *Organometallics*, **1983**, *2*, 1635.

2.2.2. $Ru_2(CO)_7(\mu\text{-dppm})$

The photochemical reaction of $Ru(CO)_4(\eta^1\text{-dppm})$, **1**, with $Ru(CO)_5$ to generate $Ru_2(CO)_7(\mu\text{-dppm})$, **2**, has been reported by our group.[9] It was noted that a trace amount of the mononuclear species, $Ru(CO)_3(\eta^2\text{-dppm})$, is also formed as a result of a side reaction,

$$\underset{\mathbf{1}}{Ru(CO)_4(\eta^1\text{-dppm})} + Ru(CO)_5 \xrightarrow[\text{pentane, RT}]{h\nu,\ \lambda \geq 280\ nm} \mathbf{2} + Ru(CO)_3(\eta^2\text{-dppm})$$

A variety of solvents for this reaction were tried,[15] but it was found that only the photolysis of a hydrocarbon solution of **1** and $Ru(CO)_5$ would yield **2**. The solubility of **1** in hydrocarbon solvents is poor (ca. 0.1 mg/ml), consequently scaling up the reaction is difficult. Also, in my hands, the formation of substantial amounts of $Ru(CO)_3(\eta^2\text{-dppm})$ (ca. 20%) was observed in the above reaction, which could not be readily separated from **2**.

Successful synthesis of **2** could also be achieved by the photolysis of the known trinuclear species $Ru_3(CO)_{10}(\mu\text{-dppm})$[9] under an atmosphere of carbon monoxide,

$$Ru_3(CO)_{10}(\mu\text{-dppm}) \xrightarrow[\text{pentane, CO}]{h\nu,\ \lambda \geq 280\ nm} \underset{\mathbf{2}}{Ru_2(CO)_7(\mu\text{-dppm})} + Ru(CO)_5$$

As above, the photochemical fragmentation of $Ru_3(CO)_{10}(\mu\text{-dppm})$ to form **2** could only be achieved using hydrocarbon solvents in which the starting material is only sparingly soluble (ca. 0.1 mg/ml). In my hands, quantitative conversion of the trinuclear starting material to give **2** and $Ru(CO)_5$ was successful, with isolated yields of **2** similar to that reported (ca. 80%).[9] However, during the isolation of **2**, which

involved removal of solvent and the $Ru(CO)_5$ generated in the reaction, small amounts of $Ru_3(CO)_{10}(\mu$-dppm) were invariably observed. The latter compound was not detected by IR spectroscopy at the end of the photoreaction, indicating that during isolation the reverse reaction between **2** and $Ru(CO)_5$, in the absence of the protective CO atmosphere, is indeed very favourable. This is in line with the known lability

$$\underset{\mathbf{2}}{Ru_2(CO)_7(\mu\text{-dppm})} + Ru(CO)_5 \xrightarrow[-2CO]{\text{vacuum}} Ru_3(CO)_{10}(\mu\text{-dppm})$$

of $Ru(CO)_5$[7a] and the great reactivity of **2** reported in this thesis. The facile formation of the trinuclear dppm complex, the apparent 'thermodynamic sink' with these compounds,[8c] also accounts for the difficulties encountered with the attempted preparation of **2** via simpler routes[9] than those finally devised. Returning to the isolation of **2** it should be noted that most of the trinuclear species could be washed away using small amounts of hydrocarbon solvent.

Detailed spectroscopic characterization of $Ru_2(CO)_7(\mu$-dppm) (Table 2.4) has been reported by our group,[9] and agrees well with the data given for the analogous diiron complex, $Fe_2(CO)_7(\mu$-dppm).[2] The crystal structure for $Fe_2(CO)_7(\mu$-dppm) is

Table 2.4: Infrared Data for $M_2(CO)_7(\mu$-dppm) Complexes (M = Fe, Ru)

Compound	IR ν_{CO} (cm^{-1})
$Ru_2(CO)_7(\mu$-dppm) **2**	2059s, 2014s, 1992s, 1957s, 1937m, 1748m [a]
$Fe_2(CO)_7(\mu$-dppm) [c]	2049s, 1994s, 1982s, 1951(sh), 1940s,1754m [b]

[a] Solvent: dichloromethane
[b] Solvent: chloroform
[c] Wegner, P. A.; Evans, L.; Haddock, J. *Inorg. Chem.*, **1975**, *14*, 192.

known.[1] The IR spectrum of **2** has a bridging carbonyl stretch at 1748 cm^{-1}, similar to that observed for the diiron complex at 1754 cm^{-1}.

The ^1H n.m.r. spectrum of **2** exhibits a multiplet centred at δ 7.35 p p.m. integrating to twenty protons relative to the triplet, due to the methylene protons, at δ 3.90 p.p.m.. The triplet is a result of coupling to the two equivalent phosphorus nuclei of the bridging dppm ligand (J_{PH} = 11.6 Hz). The equivalence of the two phosphorus nuclei is confirmed by the presence of only one signal, a singlet, at δ 35.3 p.p.m. in the $^{31}P\{^1H\}$ n.m.r. spectrum (Table 2.5).

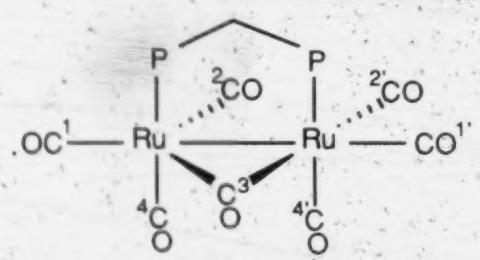
Table 2.5: ^1H and $^{31}P\{^1H\}$ n.m.r. Data for $M_2(CO)_7(\mu\text{-dppm})$ Complexes (M = Fe, Ru)

Compound	N.M.R. data δ (p.p.m.)[a]	
	^1H	$^{31}P\{^1H\}$
$Ru_2(CO)_7(\mu\text{-dppm})$ **2**[e]	7.35 m (20H) [b] 3.57 t (2H, J_{PH} = 11.6)	35.3 s [b]
$Fe_2(CO)_7(\mu\text{-dppm})$ [f]	7.22 m (20H) [c] 3.54 t (2H, J_{PH} = 11)	62.6 [d,g]

[a] Coupling constants reported in Hz
[b] Solvent: dichloromethane-d_2
[c] Solvent: dichloromethane
[d] Solvent: chloroform-d
[e] Cf. Kiel, G.-Y.; Takats, J. *Organometallics*, **1989**, *8*, 839, and this work.
[f] Wegner, P. A.; Evans, L.; Haddock, J. *Inorg. Chem.*, **1975**, *14*, 192.
[g] Hogarth, G. *PhD Thesis*, University of Bristol, **1986**, p. 233.

The $^{13}C\{^1H\}$ n.m.r. spectrum of **2** exhibits a single peak at room temperature in the carbonyl region. Fluxional behaviour of the carbonyl ligands was anticipated from a previous report on the analogous iron derivative.[1] In this case, however, the facility of the process was such that the single, averaged peak persisted down to the

lowest recorded temperature, 173 K. In contrast to the iron complex the ^{13}C n.m.r. spectrum of **2** at 203 K exhibits two signals in a 5:2 intensity ratio, indicating that



local carbonyl scrambling at each ruthenium centre has been stopped, while a rapid "merry-go-round" carbonyl exchange between the two metal centres is still occurring between CO ligands 1, 1', 2, 2', and 3. At 203 K the resonance assigned to carbonyl ligands 4 and 4' exhibits an AA'XX' pattern. A computer assisted simulation this pattern allowed the P-C coupling to be calculated (J_{PC} = 80.3 Hz), a coupling that is indicative of one CO *trans* to each phosphorus atom.

2.3. Synthesis and Characterization of $Ru(CO)_4(\eta^1$-dmpm) and $Ru_2(CO)_7(\mu$-dmpm)

2.3.1. $Ru(CO)_4(\eta^1$-dmpm)

Thermal reaction of dmpm with the known "$Ru(CO)_4$" transfer reagents $Ru(CO)_5$,[7a] $Ru(CO)_4(\eta^2\text{-}C_2H_4)$,[7a] $Ru(CO)_4(\eta^2\text{-}CH_2CHCO_2CH_3)$,[7b] and $Ru(CO)_4(\eta^2\text{-}CH_2CHCH_3)$[9] all appeared to give $Ru(CO)_4(\eta^1$-dmpm), **3**, as one of the products based on monitoring the progress of the reaction by IR. However, at room temperature the reactions were very slow and extensive formation of the thermodynamically more stable complexes $Ru_3(CO)_8(\mu\text{-dmpm})_2$,[16] **5**, and $Ru_2(CO)_5(\mu\text{-dmpm})_2$,[17] **6**, occurred also. Complexes **5** and **6** have been identified by comparison of their IR and ^{31}P n.m.r. spectra with those reported in the

literature.[16,17] The IR spectrum of **5** obtained in this study exactly matches that reported by Smith,[16a] but differs in minor ways from those reported by Puddephatt[16b] and Haines.[16c] Reaction of dmpm with $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ was the most facile and gave the highest yield of **3** in solution. Work-up and attempts to isolate **3** were fraught with difficulties. Apparently **3** readily undergoes rapid disproportionation to give either **5**, **6**, or a mixture of both (*vide supra*).

In an effort to speed the formation of **3**, and thereby reduce formation of secondary products, attempts have been made to react $Ru(CO)_5$ with dmpm in the presence of trimethylamine-N-oxide, $(CH_3)_3NO$. This reaction was no more rapid than the reaction using $Ru(CO)_4(\eta^2\text{-}C_2H_4)$, and the mixed solvent system required for the dissolution of $(CH_3)_3NO$ in the hydrocarbon solution of $Ru(CO)_5$ served only to enhance the difficulties experienced during the workup.

Since isolation of pure **3** proved difficult, attempts were made to identify and to characterize it in solution as it formed. The IR spectrum of an aliquot of the solution from the reaction between $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ and dmpm showed the typical four band pattern of an $M(CO)_4(\eta^1\text{-}L_2)$ species (M = Fe, L_2 = dppm, dppe;[12] M = Ru, L_2 = dppm[9]), where the η^1-bound diphosphine ligand occupies the axial position of a trigonal bipyramid. The carbonyl stretching frequencies at 2061s, 1986m, 1950(sh), 1945s agree well with those reported[9] for the dppm analogue, **1** (Table 2.2). Small amounts of a secondary product could also be seen in the IR spectrum and was tentatively assigned to $Ru(CO)_3(\eta^2\text{-dmpm})$, **7**, by comparison of its

$$Ru(CO)_4(\eta^2\text{-}C_2H_4) + \text{dmpm} \xrightarrow{\text{pentane, RT}} \underset{\mathbf{3}}{Ru(CO)_4(\eta^1\text{-dmpm})} + \underset{\mathbf{7}}{Ru(CO)_3(\eta^2\text{-dmpm})}$$

spectrum with those of analogous dppm complexes (Table 2.6). Complex **7** has carbonyl stretching frequencies at 1963m, 1930s, 1907s cm^{-1}, which are similar to

those observed for $Fe(CO)_3(\eta^2\text{-dppm})$[2] (1989s, 1919m, 1909s cm^{-1}) and $Ru(CO)_3(\eta^2\text{-dppm})$[15] (2011s, 1946s, 1937s cm^{-1}).

The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of crude **3** also showed that the sample was contaminated with a secondary product. Three signals were observed in the $^{31}P\{^1H\}$ n.m.r. spectrum: two doublets and a singlet. The two doublets, located at δ 33.6 and 8.2 p.p.m. (J_{PP} = 19.5 Hz) have the same integral and are indicative of two inequivalent phosphorus nuclei of an asymmetrically bound dmpm ligand. The singlet, located at δ 7.7 p.p.m., has a integral that is different from those measured for the two doublets and suggests the presence of a second product containing a symmetrically bound dmpm ligand.

Table 2.6: Infrared Data for Selected dmpm Derivatives of Ruthenium Carbonyls

Compound	IR ν_{CO} (cm^{-1})
$Ru(CO)_4(\eta^1\text{-dmpm})$ **3**	2061s, 1986m, 1950(sh), 1945s [a]
$Ru(CO)_3(\eta^2\text{-dmpm})$ **7**	1963m, 1930s, 1907s [a]
$Ru_3(CO)_8(\mu\text{-dmpm})_2$[d] **5**	2029m, 1950vs, 1924(sh), 1881w [b]
$Ru_2(CO)_5(\mu\text{-dmpm})_2$[e] **6**	1952s, 1916s, 1891s, 1875(sh), 1693m [c]

[a] Solvent: pentane
[b] Solvent: dichloromethane
[c] Solvent: benzene
[d] Cf. Clucas, J.; Foster, D.; Harding, M.; Smith, A. K. *J. Chem. Soc. Dalton Trans.*, **1987**, 277.
[e] Cf. Johnson, K. A.; Gladfelter, W. L. *Organometallics*, **1989**, *8*, 2866.

For the asymmetric dmpm species the two sets of methyl groups bound to the phosphorus atoms must also be inequivalent and so we would anticipate the presence of two doublets in the ^1H n.m.r. spectrum. Indeed, two doublets with equal integrals

are observed in the methyl region at δ 1.54 and 0.77 p.p.m.. By comparison of the integral ratios of the two doublets with the other ^1H n.m.r. signals an assignment can be made for the two methylene protons, which are observed as a doublets of doublets at δ 1.60 p.p.m.. The n.m.r. spectral data for this asymmetric species appear to be consistent with the proposed product **3** (Table 2.7). However, free dmpm has a ^{31}P resonance at δ -55.6 p.p.m., while the analogous "Fe(η^1-dmpm)" complexes, *cis*-Fe(CO)$_2$(η^2-dmpm)(η^1-dmpm)[18a] and Fe(η^2-dmpm)$_2$(η^1-dmpm),[18a] show ^{31}P resonances due to uncoordinated phosphorus atoms at δ -58.7 and -61.0 p.p.m. respectively. The oxidized phosphine of $Me_2PCH_2P(O)Me_2$ resonates at δ 35.0 p.p.m.,[18b] and so it is possible that for **3** the phosphorus atom coordinated to ruthenium resonates at δ 8.2 p.p.m. while the free phosphorus atom has been oxidized and so it resonates at δ 33.6 p.p.m..

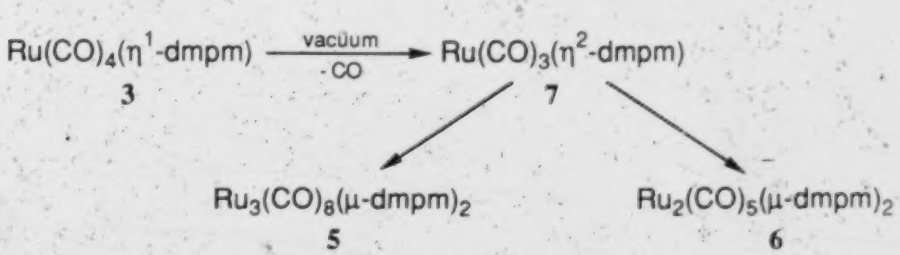
Table 2.7: ^1H and $^{31}P\{^1H\}$ n.m.r. Data for Selected dmpm Derivatives of Ruthenium Carbonyls

Compound	N.M.R. data δ (p.p.m.)[a]	
	^1H	$^{31}P\{^1H\}$
$Ru(CO)_4(\eta^1\text{-dmpm})$ **3**[e]	1.60 dd (2H, $J_{PH} = J_{P'H} = 9.9$) 1.54 d (6H, $J_{PH} = 9.8$) 0.77 d (6H, $J_{PH} = 12.3$)[b]	33.6 d ($J_{PP} = 19.5$) 8.2 d ($J_{PP} = 19.5$)[b]
$Ru(CO)_3(\eta^2\text{-dmpm})$ **7**	2.05 t (2H, $J_{PH} = 9.7$) 1.14 m (12H)[b]	7.7 s[b]
$Ru_2(CO)_5(\mu\text{-dmpm})_2$[d] **6**	1.98 quin (2H, $J_{PH} = 4.5$)[c] 1.57 t (12H, $J_{PH} = 3$)	10.5 s[c]

[a] Coupling constants reported in Hz
[b] Solvent: benzene-d_6
[c] Solvent: dichloromethane-d_2
[d] Cf. Johnson, K. A.; Gladfelter, W. L. *Organometallics*, **1989**, *8*, 2866.
[e] The n.m.r. data may refer to $Ru(CO)_4[\eta^1\text{-}Me_2PCH_2P(O)Me_2]$ due to oxidation of **3** during preparation and/or running of the n.m.r. spectrum.

The presence of a second product has already been established in the $^{31}P\{^1H\}$ n.m.r. spectrum. In agreement with the ^{31}P n.m.r. spectrum all of the methyl groups on the dmpm ligand must be equivalent. On this basis we would expect only two other signals to be present in the ^1H n.m.r. spectrum. The ^1H n.m.r. spectrum exhibits two signals, a triplet at δ 2.05 p.p.m. and a multiplet at δ 1.14 p.p.m., that have an integral ratio of 1:6 repectively. These data suggest that the second product may indeed be $Ru(CO)_3(\eta^2\text{-dmpm})$, **7**. However, the chemical shift in the ^{31}P n.m.r. spectrum assigned to **7** (δ 7.7 p.p.m.) is in sharp contrast with the chemical shifts observed for η^2-bound diphosphines of the analogous complexes $Ru(CO)_3(\eta^2\text{-dppm})$[15] (δ -15.7 p.p.m.), *cis*-$Fe(CO)_2(\eta^2\text{-dmpm})(\eta^1\text{-dmpm})$[18a] (δ -6.3 p.p.m.), and $Fe(\eta^2\text{-dmpm})_2(\eta^1\text{-dmpm})$[18a] (δ -12.2 p.p.m.). There is no satisfactory explanation that we can offer for this apparent anomaly.

Based on these results it would appear that $Ru(CO)_4(\eta^1\text{-dmpm})$ may be converted to either **5** or **6** via the intermediate $Ru(CO)_3(\eta^2\text{-dmpm})$. In a separate experiment, photolysis of $Ru(CO)_5$ in the presence of one equivalent of dmpm gave a unique product whose IR spectrum was identical to that assigned to **7**. When allowed to stand in the dark this solution precipitated a red-orange solid identified initially by its IR spectrum as the trinuclear complex **5**, and later confirmed by its $^{31}P\{^1H\}$ n.m.r. spectrum which shows the characteristic AA'BB' pattern centred at δ -8.7 p.p.m..[16a,b] Loss of CO with concomitant intramolecular attack of the uncoordinated phosphorus of **3** on the metal centre could lead to the formation of a transient η^2-dmpm complex, **7**. The ring strain caused by a chelating dmpm ligand may result in a



facile ring opening and formation of the tri- and dinuclear species **5** and **6** respectively.

2.3.2. $Ru_2(CO)_7(\mu\text{-dmpm})$

The synthesis of $Ru_2(CO)_7(\mu\text{-dmpm})$, **4**, by reacting $Ru(CO)_4(\eta^1\text{-dmpm})$, **3**, with $Ru(CO)_5$, was attempted by both thermal and photochemical routes. The thermal reaction led to the formation of the known trinuclear species $Ru_3(CO)_8(\mu\text{-dmpm})_2$[16a] and $Ru_3(CO)_{12}$.

Initial attempts in photolyzing $Ru(CO)_5$ in the presence of **3** at room temperature yielded mixtures of products, including what appeared to be **4** in very low yield. The major product in this reaction was the known trinuclear compound, $Ru_3(CO)_8(\mu\text{-dmpm})_2$, as identified by its IR spectrum in the carbonyl stretching region.[16a] However, from these experiments it was determined that **4** was only sparingly soluble in hydrocarbon solvents, as it precipitated from the reaction solution at ambient temperature. Since it was also known that the trinuclear compound $Ru_3(CO)_8(\mu\text{-dmpm})_2$ forms readily at room temperature, we reasoned that low temperature photolysis will have the dual benefit of minimizing formation of the undesired trinuclear byproduct and of causing more complete precipitation of **4**. Indeed, such a reaction gave a larger isolated yield of crude **4** (36%), but unfortunately did not completely eliminate side reactions.

$$\underset{\mathbf{3}}{Ru(CO)_4(\eta^1\text{-dmpm})} + Ru(CO)_5 \xrightarrow[\text{pentane, CO, -20 °C}]{h\nu,\ \lambda \geq 280\ nm} \underset{\mathbf{4}}{Ru_2(CO)_7(\mu\text{-dmpm})} + \ldots$$

The synthesis of **4** remains problematic. A large part of this stems from the difficulties in isolating pure **3**. As a result the preparation of **4** involves *in situ*

generation of **3** with all the inherent problems with minor amounts of impurities and the difficult task of matching the stoichiometry of **3** and $Ru(CO)_5$. So far we have not been able to isolate **4** in pure form.

Photolysis of an approximate one to one mixture of $Ru(CO)_4(\eta^1$-dmpm) and $Ru(CO)_5$ in pentane at -20°C leads to the precipitation of **4** from solution. The IR spectrum of **4** (Table 2.8) in the carbonyl region has a pattern similar to that observed for $Fe_2(CO)_7(\mu$-dmpm);[6] note the bridging carbonyl stretch at 1736 cm^{-1}.

Table 2.8: Infrared Data for $M_2(CO)_7(\mu$-dmpm) Complexes (M = Fe, Ru)

Compound	IR ν_{CO} (cm^{-1})[a]
$Ru_2(CO)_7(\mu$-dmpm) **4**	2057s, 2012s, 1988s, 1954s, 1936(sh), 1736m
$Fe_2(CO)_7(\mu$-dmpm) [b]	2044s, 1986s, 1972s, 1937s, 1745m

[a] Solvent: dichloromethane.
[b] King, R. B.; RaghuVeer, K. S. *Inorg. Chem.*, **1984**, *23*, 2482.

The ^1H n.m.r. spectrum agrees well with the data reported by King[6a] for the analogous $Fe_2(CO)_7(\mu$-dmpm) complex. The hydrogen atoms of the four methyl groups appear as an apparent triplet at δ 1.64 p.p.m., a position that is virtually identical to that observed for the iron analogue[6a] at δ 1.62 p.p.m. (Table 2.9). The equivalence of all four methyl groups is due to the fluxional behaviour of the carbonyl ligands, and the triplet appearance is a consequence of virtual coupling to the chemically equivalent but magnetically non-equivalent phosphorus nuclei. The two methylene protons of dmpm also appear as a triplet, and show coupling to phosphorus. The methylene signals appear at δ 1.95 p.p.m. (J_{PH} = 10.8 Hz) for **4**.

and at δ 2.03 p.p.m. (J_{PH} = 11 Hz)[6a] for the iron analogue. Haines has also reported limited spectroscopic data for the diiron complex.[6b]

The $^{31}P\{^1H\}$ n.m.r. spectrum exhibits a major singlet at δ 8.7 p.p.m., corroborating the equivalence of the phosphorus nuclei. However, as can be seen in

Table 2.9: ^1H and $^{31}P\{^1H\}$ n.m.r. Data for $M_2(CO)_7(\mu\text{-dmpm})$ Complexes (M = Fe, Ru)[a]

Compound	N.M.R. data δ (p.p.m.)	
	^1H	$^{31}P\{^1H\}$
$Ru_2(CO)_7(\mu\text{-dmpm})$ **4**	1.95 t (2H, J_{PH} =10.8) [b] 1.64 t (12H, J_{PH} = 4.7)	8.7 s [b]
$Fe_2(CO)_7(\mu\text{-dmpm})$ [d]	2.03 t (2H, J_{PH} =11) [c] 1.62 t (12H, J_{PH} = 4)	42.8 s [c]

[a] Coupling constants reported in Hz
[b] Solvent: dichloromethane-d_2
[c] Solvent: dichloromethane
[d] King, R. B.; RaghuVeer, K. S. *Inorg. Chem.*, **1984**, *23*, 2482.

Table 2.9 its position is some 34.1 p.p.m. to the high field of the analogous iron complex. Although this chemical shift may appear to be large, it may be rationalized by comparing the differences in ^{31}P chemical shifts between analogous iron and ruthenium complexes as the metal and ligands are changed in a systematic fashion. The ^{31}P chemical shifts in $Fe_2(CO)_5(\mu\text{-dmpm})_2$[6a] and $Ru_2(CO)_5(\mu\text{-dmpm})_2$[17] are at δ 7.9 and 10.5 p.p.m. respectively, establishing an upfield shift of Δδ = 37.4 p.p.m. when the metal is changed from Fe to Ru. Similarily in $[\{Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}1,10\ phen)\}_2(\mu\text{-}L_2)]^{2+}$ (L_2 = dppm, dmpm)[19] the ^{31}P chemical shift is δ 47.39 p.p.m. for dppm and δ 17.49 p.p.m. for dmpm complexes, showing that the chemical shift of

the more basic alkyl diphosphine is upfield by some ($\Delta\delta$) 31.9 p.p.m.. With this information in hand it is clear that the observed changes between $Ru_2(CO)_7(\mu$-dppm), **2**, and $Ru_2(CO)_7(\mu$-dmpm), **4**, (δ 35.3 and 8.7 p.p.m. respectively; $\Delta\delta$ = 26.6 p.p.m.), and the changes between $Ru_2(CO)_7(\mu$-dmpm) and $Fe_2(CO)_7(\mu$-dmpm)[6a] (δ 8.7 and 42.8 p.p.m. respectively; $\Delta\delta$ = 31.9 p.p.m.), are in fact in the anticipated range.

2.4. Experimental Section

2.4.1. Solvents and General Techniques

Solvents listed in Table 2.10 were dried by refluxing over the appropriate drying agent under a nitrogen atmosphere, and distilled just prior to use. Methylcyclohexane and ethanol (98%) were dried over molecular sieves. When necessary, solvents were degassed before use by repeated freeze-pump-thaw cycles. Before being refluxed and distilled, pentane and hexane were preconditioned by successive washings with concentrated H_2SO_4 until no colour appeared in the acid layer, followed by washing with an aqueous solution of Na_2CO_3, and finally by drying over Na_2SO_4. Deuterated solvents were stored over molecular sieves under an atmosphere of dry nitrogen or argon.

Table 2.10: Drying Agents Used for Solvents

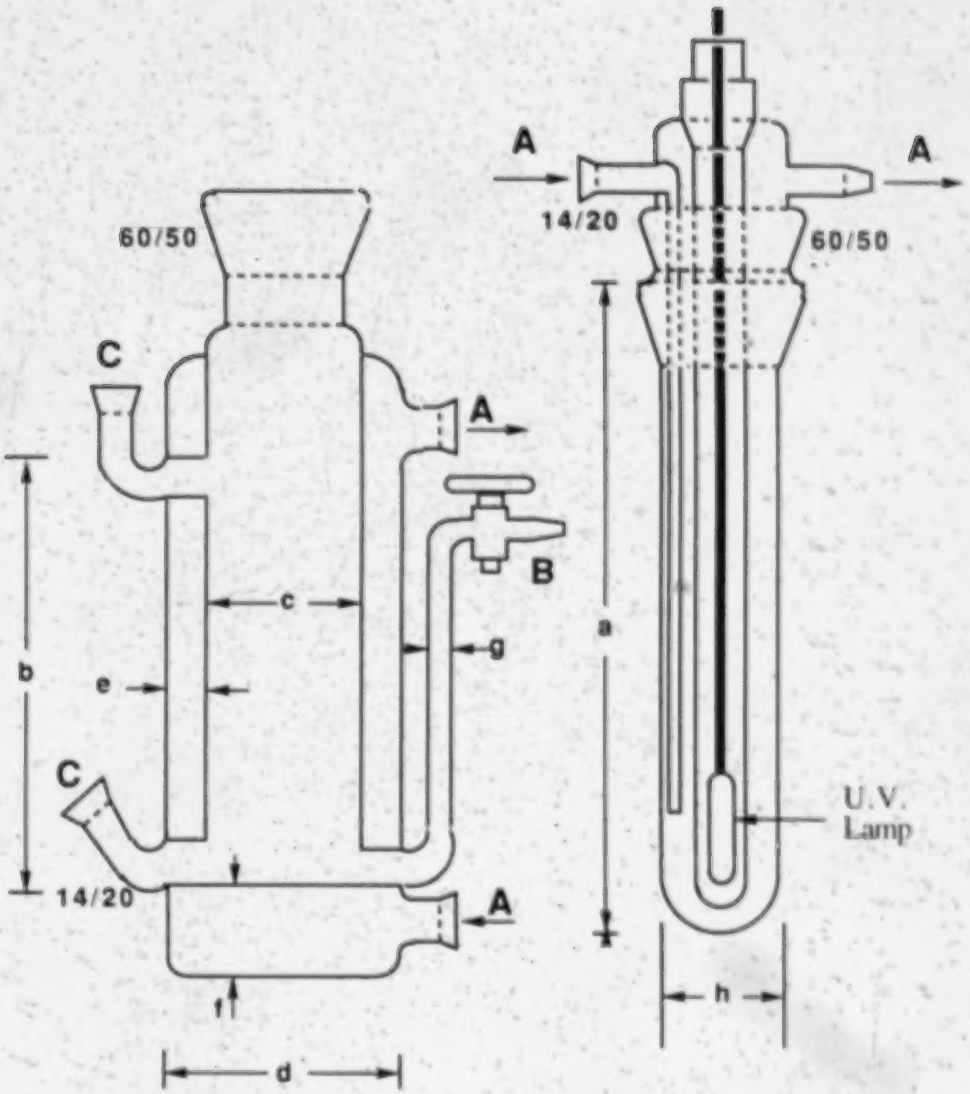
Solvent	Drying Agent
Toluene	Sodium metal
N-pentane	Calcium hydride
Diethylether	Sodium-potassium alloy/benzophenone
Benzene	Potassium metal
N-hexane	Potassium metal
Tetrahydrofuran	Potassium metal/benzophenone
Dichloromethane	Phosphorus pentoxide

Glassware was washed in a KOH-Ethanol (95%) solution and dried in an oven at 120°C before use. All experimental procedures were performed in standard Schlenk vessels using standard Schlenk techniques under purified inert atmospheres of either nitrogen or argon. Purification of nitrogen or argon was accomplished by passing the commercial gas through a heated column (100°C) of BASF Cu-based catalyst (R3-11) to remove oxygen, and a column of Mallinkrodt Aquasorb (P_2O_5 on an inert support) to remove water. Ultrahigh purity (U.H.P.) carbon monoxide and hydrogen gases were used as received. Acetylene gas was passed through a cold trap (Dry Ice/acetone) to remove acetone stabilizer. All other commercial grade gases were used as received.

2.4.2. Photochemical Techniques

Photochemical experiments were performed using the apparatus illustrated in Figure 2.1 which consists of an outside cooling jacket, with a gas inlet and two ports, and a cooling insert into which the lamp is placed. Cut-off filters were fashioned from either Pyrex glass ($\lambda_{max} \geq 280$ nm) or GWV (Glasswerk Wertheim) glass ($\lambda_{max} \geq 370$ nm). The u.v. source was a Philips HPK 125 Watt Mercury Vapour lamp. The complete Immersion Well, consisting of the cooling jacket and the insert, was used with the appropriate cut-off filter for internal photolysis. A methanol circulating/cooling bath was used to maintain the reaction solution at a constant temperature during the experiment and to keep the lamp cool. The insert was used alone, with the appropriate cut-off filter, for external photolysis. A sample solution was held in a Schlenk tube positioned beside the insert. Tap water was used to cool the lamp.

Figure 2.1: Immersion Well



A	inlet/outlet ports for cooling	**a** 29.0 cm	**e** 1.0 cm
B	gas inlet	**b** 25.0 cm	**f** 1.0 cm
C	sample ports	**c** 6.5 cm	**g** 0.5 cm (id)
		d 8.5 cm	**h** 4.5 cm

2.4.3. Physical Measurements

Infrared spectra were obtained over the range 2200-1600 cm^{-1} using either a Nicolet MX-1 or a Bomem MB-100 Fourier Transform Interferometer. Solution samples and solvent background were held between either KBr (0.1 mm or 0.5 mm path lengths) or CaF_2 (0.1 mm path length) plates. ^{1}H, ^{31}P, and ^{13}C n.m.r. spectra were obtained on either a Bruker WH-200 (^{1}H), a WM-360 (^{1}H,^{13}C), or a WP-400 ($^{31}P\{^{1}H\}$, $^{1}H\{^{31}P\}$) Fourier Transform (FT) Spectrometer. Overnight ^{13}C n.m.r. spectra were collected on a Bruker AM-300 FT spectrometer, and variable temperature ^{13}C n.m.r. experiments were carried out on the Bruker WM-360 FT spectrometer. Chemical shifts, δ (p.p.m.), are reported relative to the solvent resonances (versus TMS) for ^{1}H and ^{13}C n.m.r. spectra, and relative to an external standard of 85% H_3PO_4 for ^{31}P spectra.

2.4.4. Starting Materials and Reagents

Dodecacarbonyltriruthenium was prepared as outlined in the literature[20] from ruthenium trichloride hydrate (Johnson Matthey Inc.). Bis(diphenylphosphino)-methane, and bis(dimethylphosphino)methane were purchased from Aldrich Chemical Company and used as received. Trimethylamine-N-oxide dihydrate was also obtained from Aldrich and was sublimed *in vacuo* at 90°C onto a cold finger prior to use. ^{13}C-enriched carbon monoxide (99.1%) was purchased from Isotec (Matheson) Inc.

2.4.5. Synthetic Procedures

Preparation of $Ru(CO)_4(\eta^1$-dppm), 1

Method a):

A slurry of $Ru_3(CO)_{12}$ (63.1 mg, 0.0987 mmole) in pentane (100 ml), held in a Schlenk tube, was degassed by two freeze-pump-thaw cycles. The solution was irradiated using a water-cooled external source ($\lambda_{max} \geq 370$ nm) until the orange-yellow solution became almost colourless. The IR spectrum at this point indicated complete conversion to $Ru(CO)_5$ with only two bands in the ν_{CO} region at 2037 and 2003 cm^{-1}. The solution of $Ru(CO)_5$ was transferred under argon to an immersion well cooled to -20°C and enough pentane was added (ca. 140 ml) so that the level of the solution extends above the lamp inside the immersion well. The entire solution (ca. 240 ml) was allowed to cool while being purged with propylene for several minutes. A moderate to rapid flow of propylene was passed through the solution while it was being irradiated ($\lambda_{max} \geq 280$ nm) at -20°C. The reaction was monitored by IR spectroscopy until all $Ru(CO)_5$ was consumed, forming $Ru(CO)_4(\eta^2$-$CH_2CHCH_3)$ which has ν_{CO} bands at 2102w, 2019s, 1993m cm^{-1}. A round bottom flask was charged with dppm (116.1 mg, 0.30 mmole) and toluene (5 ml) under an argon atmosphere, and was cooled to 0°C. The $Ru(CO)_4(\eta^2$-$CH_2CHCH_3)$ solution was transferred to the round bottom flask and the mixture stirred in the dark at 0°C for one to two hours until conversion to $Ru(CO)_4(\eta^1$-dppm) was complete. The solvent was removed *in vacuo* at 0°C to yield $Ru(CO)_4(\eta^1$-dppm) as a yellow-white solid, slightly contaminated with free dppm. Yield: 70%.

Method b):

A mixture of $(CH_3)_3NO$ (18.2 mg, 0.243 mmole) and dppm (94.7 mg, 0.246 mmole) in THF:98% ethanol (34 ml:17ml) was degassed by three freeze-pump-thaw

cycles. The solution was placed under a CO atmosphere and cooled to 0°C. $Ru(CO)_5$ (0.247 mmole), generated *in situ* by external irradiation of a slurry of $Ru_3(CO)_{12}$ (52.7 mg, 0.0824 mmole) under a CO atmosphere ($\lambda_{max} \geq 370$ nm), was transferred under CO to the $(CH_3)_3NO$/dppm solution. The reaction mixture was stirred in the dark at 0°C for four hours. The solution was filtered and the solvent was removed *in vacuo* at 0°C. The resulting yellow solid was washed with pentane (2-5 ml) and dried to give a yellow powder of $Ru(CO)_4(\eta^1$-dppm) (105 mg, 71%), slightly contaminated with free dppm.

Analysis Calculated for $C_{37}H_{38}O_6P_2Ru$: C, 59.92%; H, 5.16%. Found: C, 60.11%; H, 5.16% [$Ru(CO)_4(\eta^1$-dppm)·2THF].

IR (pentane, ν_{CO}): 2061s, 1989m, 1956s, 1944s cm^{-1}.

^1H n.m.r. (298 K, CD_2Cl_2): δ 7.4 (m, 20H, C_6H_5), 3.33 (dd, 2H, CH_2, J_{PH} = 9.0 Hz).

$^{31}P\{^1H\}$ n.m.r. (298 K, CD_2CL_2): δ 38.3 (d, Ru-P, J_{PP} = 97.6 Hz), -26.2 (d, Free, J_{PP} = 97.6 Hz).

Preparation of $Ru_2(CO)_7(\mu$-dppm), 2

Method a):

$Ru_3(CO)_{10}(\mu$-dppm) was prepared according to the method outlined in the literature.[8b] $Ru_3(CO)_{10}(\mu$-dppm) (23.7 mg, 0.0245 mmole) in pentane (160 ml) was degassed by two freeze-pump-thaw cycles, and then transferred under a CO atmosphere to the immersion well. The solution was purged with CO for 10 minutes, then it was irradiated for 4.5 hours at 18°C ($\lambda_{max} \geq 280$ nm). Complete reaction was confirmed by the absence of the ν_{CO} band of $Ru_3(CO)_{10}(\mu$-dppm) at 2078 cm^{-1} in the IR spectrum. The solution was transferred under a CO atmosphere to a flask cooled to -78°C. The solvent was removed *in vacuo* below -40°C. The residue was washed

with pentane (2-3 ml) at -78°C and dried *in vacuo* below -40°C to give $Ru_2(CO)_7(\mu$-dppm) as a yellow solid in 80% yield. Contamination with trace amounts of $Ru_3(CO)_{10}(\mu$-dppm) was visible in the IR spectrum.

Analysis Calculated for $C_{32}H_{22}O_7P_2Ru_2$: C, 49.1%; H, 2.83%. Found: C, 48.25%; H, 2.25%.

IR (CH_2Cl_2, ν_{CO}): 2059s, 2014s, 1992s, 1957s, 1937m, 1748m cm^{-1}.

^1H n.m.r.(298 K, CD_2Cl_2): δ 7.35 (m, 20H, C_6H_5), 3.57 (t, 2H, CH_2, J_{PH} = 11.6 Hz).

$^{31}P\{^1H\}$ n.m.r. (298 K, CD_2Cl_2): δ 35.3 (s).

$^{13}C\{^1H\}$ n.m.r. (293 K, CD_2Cl_2): δ 211.8 (s[br], 6CO), 128-135 (m, phenyl), 40.7 (t, CH_2, J_{PC} = 23 Hz); (173 K, CD_2Cl_2, CO region only): δ 216.2 (s[br], 4CO), 198.7 (AA'XX', 2CO, $J_{PC'}$ = 7.7, J_{PC} = 80.3, J_{PP} = 97.5 Hz).

Method b):

$Ru(CO)_4(\eta^1$-dppm) (33.2 mg, 0.0556 mmole) in pentane (150 ml) was degassed by two freeze-pump-thaw cycles, and then transferred under a CO atmosphere to the immersion well. $Ru(CO)_5$ (0.0591 mmole), generated *in situ* by external irradiation of $Ru_3(CO)_{12}$ (12.6 mg, 0.0197 mmole) in pentane (12 ml) under a CO atmosphere ($\lambda_{max} \geq 370$ nm), was transferred under CO to the $Ru(CO)_4(\eta^1$-dppm) solution. The reaction mixture was irradiated for 10 to 15 minutes at room temperature ($\lambda_{max} \geq 280$ nm). A precipitate formed. The solution was inverse filtered under a CO atmosphere to a flask cooled to -78°C. The solvent was removed *in vacuo* below -40°C. The residue was washed with pentane at -78°C and dried *in vacuo* below -40°C to yield a yellow solid of $Ru_2(CO)_7(\mu$-dppm) (ca.70%) contaminated with $Ru(CO)_3(\eta^2$-dppm) (ca. 30%).

Preparation of $Ru(CO)_4(\eta^1$-dmpm), 3

Dmpm (70.0 µl, 0.462 mmole) in pentane (7 ml) was cooled to 0°C. $Ru(CO)_4(\eta^2$-$C_2H_4)$ (0.465 mmole), generated *in situ* by external irradiation of a slurry of $Ru_3(CO)_{12}$ (99.0 mg, 0.155 mmole) in pentane (100 ml) under an ethylene atmosphere ($\lambda_{max} \geq 370$ nm), was transferred under an argon atmosphere to the dmpm solution. The reaction mixture was stirred in the dark at room temperature for eight hours. Complete reaction was confirmed by the absence of the ν_{CO} bands of $Ru(CO)_4(\eta^2$-$C_2H_4)$ at 2105w, 2023m, 1990vs cm^{-1} in the IR spectrum. Attempts to isolate **3** by removing the solvent *in vacuo*, even at low temperature (-78°C), or by precipitation from solution at low temperature (-100°C), led only to mixtures of solid products. The major component is believed to be **3**, whose spectroscopic characteristics are listed below:

IR (pentane, ν_{CO}): 2061s, 1986m, 1950(sh), 1945s cm^{-1}.

^1H n.m.r. (298 K, C_6D_6): δ 1.66 (dd, 2H, CH_2, J_{PH} = 9.9 Hz), 1.54 (d, 6H, CH_3, J_{PH} = 9.8), 0.77 (d, 6H, CH_3, J_{PH} = 12.3 Hz).

$^{31}P\{^1H\}$ n.m.r. (298 K, C_6D_6): δ 33.6 (d, Ru-P, J_{PP} = 19.5 Hz), 8.2 (d, Free, J_{PP} = 19.5 Hz).

Preparation of $Ru_2(CO)_7$(µ-dmpm), 4

A solution of $Ru(CO)_4(\eta^1$-dmpm) was generated from $Ru(CO)_4(\eta^2$-$C_2H_4)$ as described above ($Ru_3(CO)_{12}$, 61.8 mg, 0.0987 mmole; dmpm, 44.0 µl, 0.291 mmole; 50 ml pentane), and was inverse filtered under CO to the cold (-20°C) immersion well . A solution of $Ru(CO)_5$, from a slurry of $Ru_3(CO)_{12}$ (48.3 mg, 0.076 mmole) in pentane (40 ml), was transferred under CO to the immersion well and enough pentane (50 ml) was added so that the level of the solution extends above the lamp in the immersion well. The pale yellow mixture was purged with CO for

five minutes and then the immersion well was closed off. The mixture was irradiated ($\lambda_{max} \geq 280$ nm) at -20°C for 40 minutes until a precipitate formed and a red-orange solution developed. The solution and precipitate were transferred under argon to a round bottom flask cooled to -78°C. The solution was then filtered, leaving behind a red precipitate. The precipitate was dried *in vacuo* at -40°C to yield $Ru_2(CO)_7(\mu$-dmpm) as a red solid (16%). Only minor contamination was evident in the ^1H and $^{31}P\{^1H\}$ n.mr. spectra.

IR (CH_2Cl_2, ν_{CO}): 2057s, 2012s, 1988s, 1954s, 1936(sh), 1736m cm^{-1}.

^1H n.m.r. (298 K, CD_2Cl_2): δ 1.95 (t, 2H, CH_2, J_{PH} = 10.8 Hz), 1.64 (t, 12H, CH_3, J_{PH} = 4.7 Hz).

$^{31}P\{^1H\}$ n.m.r. (298 K, CD_2Cl_2): δ 8.7 (s).

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Chapter Three

Synthesis, Characterization, and Reactivity of $Ru_2(CO)_6(H)_2(\mu\text{-dppm})$

3.1. Introduction

The binding of dihydrogen to a transition metal centre is a key step in the homogeneous hydrogenation of an unsaturated organic substrate catalyzed by transition metal complexes,[1] and is thought to precede the reduction of polar molecules such as CO on a metal surface in the Fischer-Tropsch synthesis.[2] The loss of a coordinated ligand may be considered as a key step in the formation of a site of coordinative unsaturation, a site that may render the metal open to attack by other ligands or substrates. Thus the loss of dihydrogen from either a coordinated η^2-dihydrogen ligand[3] or a dihydride[4] would leave a vacant site on the metal that may be open to attack by such substrates as olefins or alkynes. Compared to monometallic complexes there is comparatively little known about catalysts containing more than one metal centre. This topic is of current interest because of the potential for cooperativity between adjacent metal centres leading to possible enhancement of catalytic activity. This goal has yet to be realized, consequently the study of dihydrogen with di- and polymetallic systems remains a worthwhile, and hopefully insightful endeavor.

The lack of attention given to dppm-bridged diruthenium complexes (see Chapter One), and the relatively few examples of a reversible thermal addition of dihydrogen to a coordinatively unsaturated dinuclear complex[5,6,7] has encouraged our investigation of this area. This chapter discusses the thermal reaction of H_2

with the complex $Ru_2(CO)_7(\mu$-dppm), and attempts to establish the structure of the resulting product. Reactivity studies on the compound and a comparison of these results with the formation and reactivity of analogous di- and trinuclear complexes are also reported.

3.2. Preparation of $Ru_2(CO)_6(H)_2(\mu$-dppm), 8

3.2.1. Synthesis and Characterization

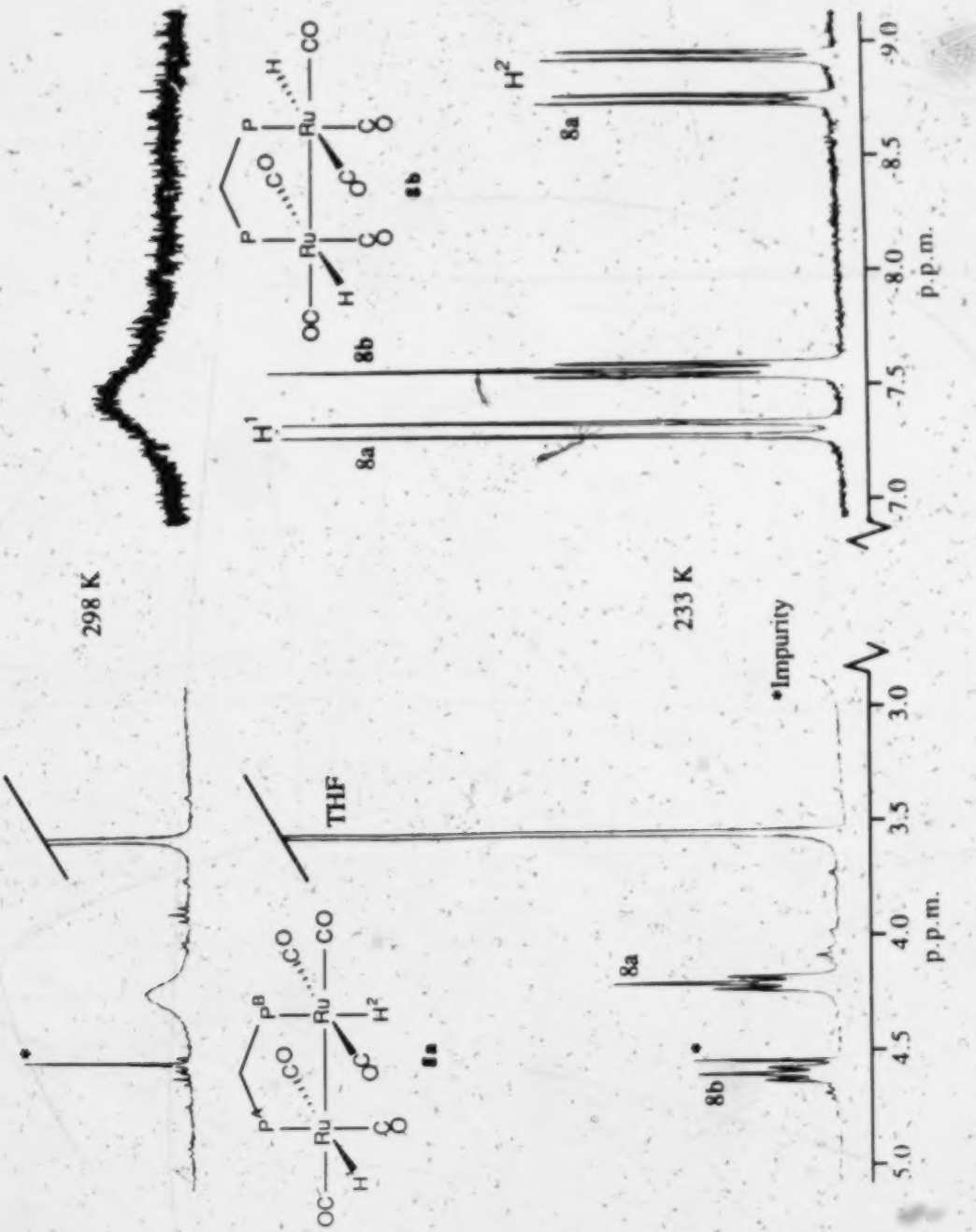
When a stream of H_2 is slowly bubbled through a THF solution of $Ru_2(CO)_7(\mu$-dppm) (**2**) the dark orange colour lightens. The progress of the reaction is monitored by IR spectroscopy and shows loss of the bridging carbonyl at 1755 cm^{-1} (ν_{CO}, THF) and the formation of new bands in the carbonyl stretching region at 2065s, 2031s, 1987(sh), 1970s,br cm^{-1}. Infrared and other spectral data led to the identification of the product as $Ru_2(CO)_6(H)_2(\mu$-dppm), **8**.

The hydrogenation product is stable in solution at room temperature under an atmosphere of H_2. However, all attempts to recover the product as a solid resulted in decomposition. Addition of CO to a solution of **8** results in rapid, quantitative regeneration of starting material **2** as evidenced by IR and ^1H n.m.r. spectroscopy. Clearly **2** and **8** are simply related via the loss of a CO ligand which is replaced by an "H_2" moiety so that eighteen electrons are maintained at both ruthenium atoms. In view of its delicate nature, **8** was characterized *in situ* by ^1H, ^{31}P and ^{13}C n.m.r. spectroscopy.

At room temperature the ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of **8** showed broad, poorly resolved signals. Cooling the sample to 243 K resulted in sharp, well resolved n.m.r. spectra (Figure 3.1). The ^1H n.m.r. spectrum (233 K)

Figure 3.1: Variable Temperature ^1H n.m.r. Spectra of **8**

Figure 3.1 · Variable Temperature ^1H n.m.r. Spectra of 8



exhibits two triplets, one at δ 4.61 and the other at δ 4.22 p.p.m., in a 1:2 integral ratio respectively. This region is typical for the methylenic protons of the dppm ligand, and suggests the presence of two compounds. Several signals are also observed at much higher field, in the terminal hydride region.[8] These high field signals consist of a doublet at δ -7.28 p.p.m., a triplet at δ -7.54 p.p.m., and a doublets of doublets at δ -8.80 p.p.m.. The $^{31}P\{^{1}H\}$ n.m.r. spectrum (233 K) shows three resonances. Two of the ^{31}P resonances are doublets, appearing at δ 38.9 (P^A) and 25.8 p.p.m. (P^B) (J_{PP} = 97.8 Hz), indicative of an asymmetric complex (**8a**), whereas the other resonance is a singlet at δ 30.0 p.p.m., indicative of a symmetric complex (**8b**). The two sets of ^{31}P resonances have an integral ratio of 2:1 (**8a**:**8b**) that remains constant over three different temperatures (193, 233, and 295 K), a ratio that is consistent with that observed in the ^{1}H n.m.r. spectrum for the two methylenic signals assigned to the different dppm ligands. On the basis of integral ratios we can assign the ^{1}H resonance at δ 4.61 p.p.m. to **8b** and the resonance at δ 4.22 p.p.m. to **8a**. Confirmation of this assignment was made by selective ^{31}P-decoupled ^{1}H n.m.r. experiments. Decoupling one or the other doublet ^{31}P resonances causes the methylene triplet at δ 4.22 p.p.m. to collapse to a doublet assigning this resonance to **8a**, while decoupling of the singlet ^{31}P resonance causes the other methylene triplet at δ 4.61 p.p.m. to collapse to a singlet assigning this resonance to **8b**.

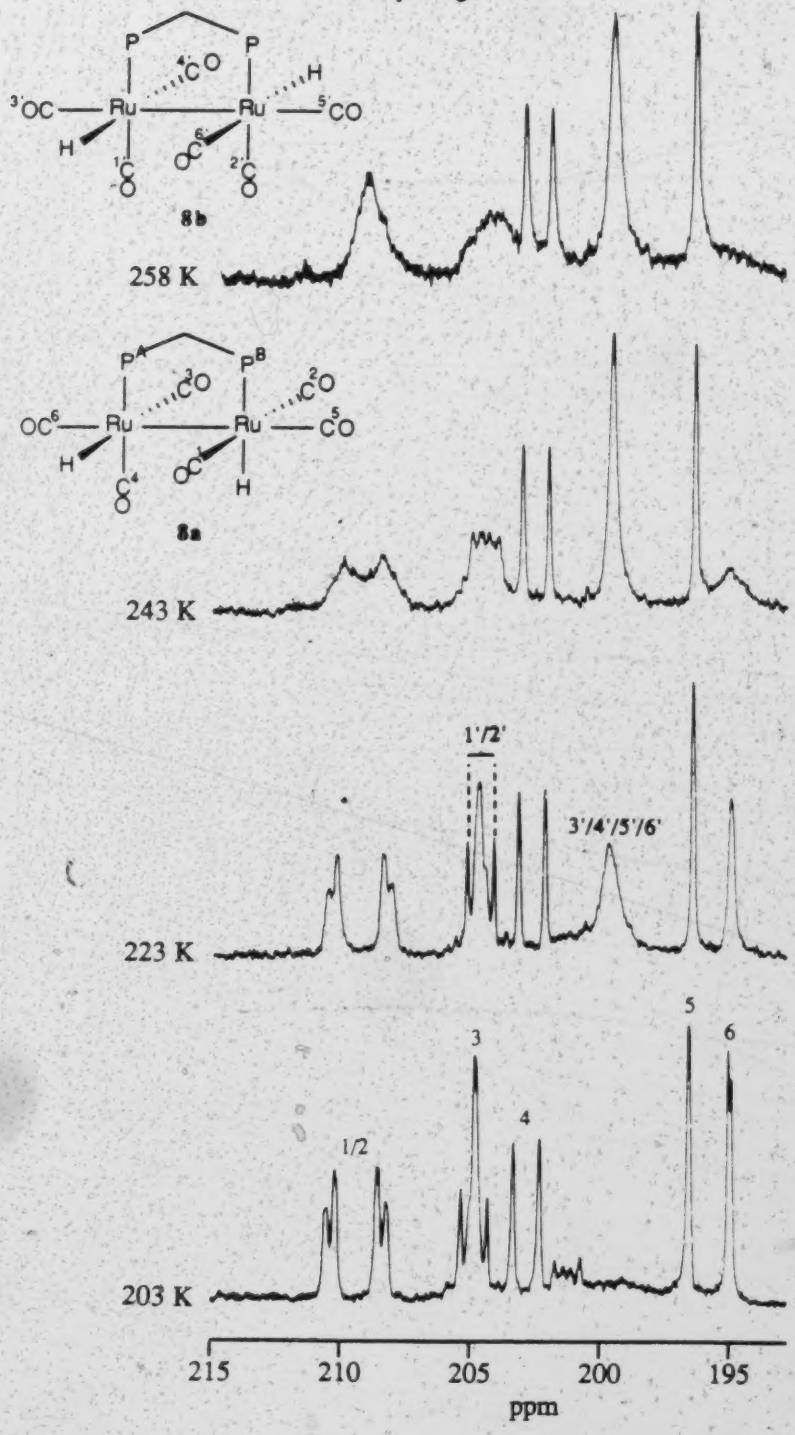
Selective ^{31}P-decoupled ^{1}H n.m.r. experiments also clearly established the assignment of the hydride resonances. Decoupling the singlet ^{31}P resonance at δ 30.3 p.p.m. causes the triplet at δ -7.54 p.p.m. to collapse to a singlet clearly assigning this hydride signal to isomer **8b** with a *cis* P-H coupling of 10.4 Hz. The remaining two hydride resonances are then assigned to **8a**, where the doublet ^{1}H resonance at δ -7.28 has a small P-H coupling constant consistent with a hydride *cis* to a phosphine[9] (J_{PHcis} = 23.2 Hz), and the ^{1}H resonance at δ -8.80

p.p.m., a doublets of doublets, has a large P-H coupling constant consistent with a hydride *trans* to a phosphorus[1,9c] ($^2J_{PHtrans}$ = 72 , $^4J_{PH}$ = 14.8 Hz). Irradiation of the doublet ^{31}P resonance of **8a** at δ 25.8 p.p.m. (P^B) causes the doublets of doublets to collapse to a triplet with a line separation of approximately 10 Hz, while leaving the doublet ^{1}H resonance at δ -7.28 p.p.m. unchanged. We were not able to fully decouple the ^{31}P resonance at δ 25.8 and so a triplet rather that the expected doublet is observed. Irradiation of the doublet ^{31}P resonance of **8b** at δ 38.8 p.p.m. (P^A) causes the doublet at δ -7.28 p.p.m. to collapse to a singlet, as well as collapsing the doublets of doublets at δ -8.80 p.p.m. to a doublet, retaining the large *trans* P-H coupling. Thus at this stage it is known that the dppm and hydride ligands of isomer **8a** have a *cis* disposition, whereas the asymmetric **8b** has one hydride ligand *cis* to one phosphorus (P^A) and one hydride ligand *trans* to the other phosphorus (P^B).

Further information about the structures of **8a** and **8b** was gathered from ^{13}C n.m.r. experiments performed on samples enriched with ^{13}CO. The $^{13}C\{^1H\}$ n.m.r. spectrum obtained at room temperature showed only a broad peak in the carbonyl region indicating that the complexes underwent some sort of carbonyl exchange processes. Cooling the sample to 223 K resulted in the appearance of a complex set of signals as shown in Figure 3.2, not unexpected when considering the presence of two isomers where one isomer is asymmetric.

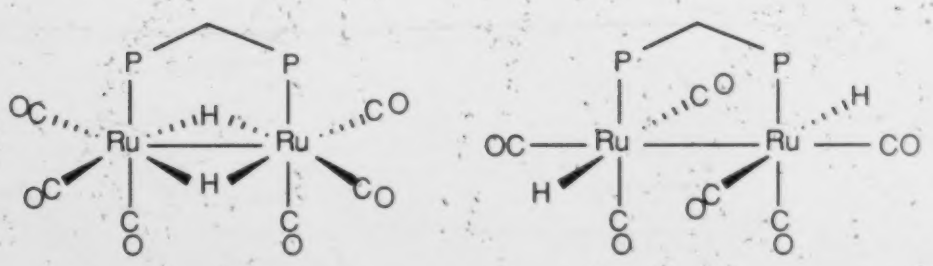
Assignment of the ^{13}C signals to individual isomers and carbonyl groups within each isomer was accomplished in stages and is based on selective ^{31}P decoupling ^{13}C n.m.r. experiments, the relative intensities of the signals, and the careful examination of line shape changes over a large temperature range. Selective ^{31}P decoupling experiments resulted in the following information about the structures of isomers **8a** and **8b**. Decoupling the phosphorus signal of the

Figure 3.2: Variable Temperature ^{13}C n.m.r. Spectra of ^{13}CO-Enriched 8, Carbonyl Region

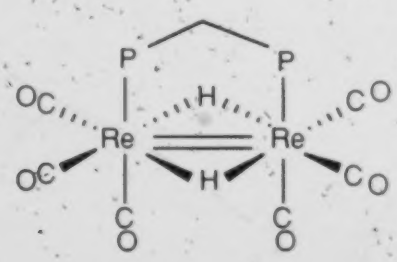


symmetric isomer **8b** caused the two outer lines of the unusual, triplet-like resonance at δ 204.6 p.p.m. to collapse. This revealed that this "triplet" signal is infact a superimposition of two separate carbonyl resonances having virtually identical chemical shifts. Thus the doublet belongs to the symmetric isomer, the large P-C coupling (J_{PC} = 91.4 Hz) indicative of a *trans* arrangement of the phosphine and carbonyl ligands. Selective decoupling of the P^A resonance of the asymmetric isomer **8a** resulted in the collapse of the doublets at δ 202.6 and 194.7 p.p.m. to singlets, allowing assignment of these signals to the asymmetric isomer where both carbonyl ligands reside on the same ruthenium centre as P^A. The large P-C coupling of 93.2 Hz indicates that this half of the molecule contains a *trans* phosphorus-carbonyl arrangement together with another carbonyl ligand *cis* to P^A (J_{PAC} = 9.2 Hz). Finally selective decoupling of P^B removed only the small coupling from the signals at δ 210.2 and 208.3 p.p.m. thus establishing that the larger splitting is due to ^{13}C-^{13}C coupling (J_{CC} ≈ 32 Hz) and that the two carbonyl groups are *trans* to one another, *cis* to P^B, and reside on the same ruthenium centre as this phosphorus donor. Having assigned four carbonyl resonances of relative intensity one to the asymmetric isomer **8a**, it is clear that the remaining two signals with the same intensity at δ 204.6 and 196.3 p.p.m. also belong to this isomer. This leaves the broad singlet at δ 199.3 p.p.m. in the ^{13}C n.m.r. spectrum at 223 K as the other signal due to the symmetric isomer **8b**. Gratifyingly this peak and the doulet at δ 204.6 p.p.m. are in the expected 2:1 ratio and together comprise approximately one half the integral intensity of the other signals assigned to **8a**, as required by the isomer ratio betwen **8a**:**8b** as established from the ^1H and $^{31}P\{^1H\}$ n.m.r. spectra.

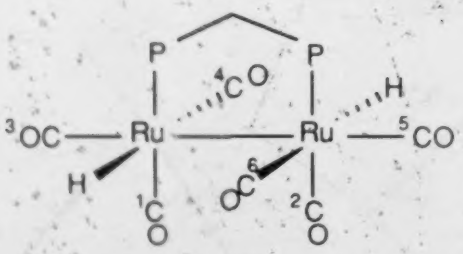
At this stage two structures can be proposed for the symmetric isomer **8b** both featuring a *cis* P-H and *trans* P-CO arrangements as established by the n.m.r.



data (*vide supra*). The structure on the left is similar to an analogous dirhenium complex, $Re_2(CO)_6(H)_2(\mu\text{-dppm})$.[4c] The carbonyls of the dirhenium complex appear as a singlet ^{13}C resonance at δ 193.4 and a doublet at δ 194.1 p.p.m. (J_{PC} = 74 Hz), integrating to four and two carbonyl ligands respectively. Therefore the structure proposed for the dirhenium complex is as illustrated below, where four



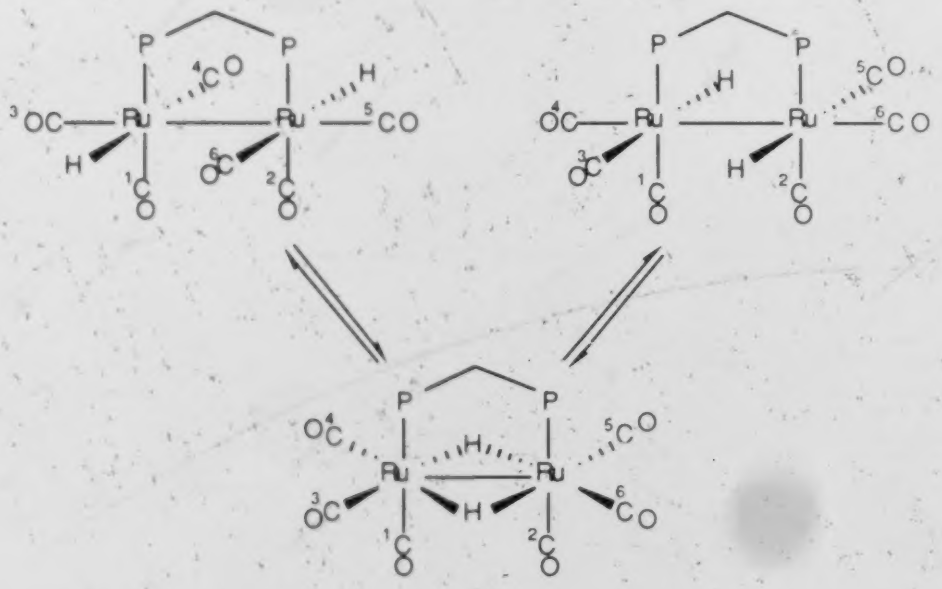
carbonyls and two bridging hydrides are in a plane perpendicular to the dppm ligand. The corresponding ^{13}C resonances of **8b** are the broad singlet at δ 199.3 p.p.m. and the doublet at δ 204.6 p.p.m. (J_{PC} = 91.4 Hz), which integrate to four and two carbonyl ligands respectively. Although this structure could accommodate the available data for **8b** it is neither in accord with the fluxional behaviour of **8b** evident in the variable temperature ^{13}C n.m.r. spectra (Figure 3.2), nor with the chemical shift of the hydride ligands which is in the region typical for a terminal hydride. Thus the alternate arrangement shown below is assigned to **8b**. Equivalence of the four carbonyl ligands is possible via the exchange shown in Scheme 3.1. The exchange proceeds via a hydride-bridged intermediate, and so the triplet appearance of the hydride signal at 233 K in the ^1H n.m.r. spectrum is due to



8b

the hydrogen coupling to two equivalent phosphorus nuclei. Therefore the observed splitting is the average of the $^{2}J_{P-H}$ and $^{4}J_{P-H}$ of the terminal Ru-H moiety. The sharpness of the carbonyl signal at 243 K in the $^{13}C\{^{1}H\}$ n.m.r. spectrum indicates that carbonyl exchange is still rapid at this temperature.

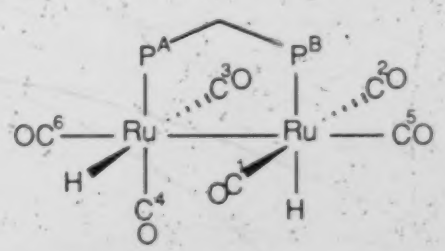
Scheme 3.1: Dynamic Behaviour of Isomer **8b**



Lowering the temperature below 243 K broadens this signal until it has merged with the baseline at 203 K. It does not reemerge even after cooling to below 183 K. Warming the sample above 243 K sharpens this singlet as the rate of carbonyl exchange in the equatorial plane increases. Above 258 K both ^{13}C signals of **8b**

start to broaden, however not before the carbonyl resonances of **8a** also start to broaden, indicating that carbonyl scrambling between the axial and equatorial carbonyls of **8b** does not occur before isomer interconversion between **8a** and **8b** renders all carbonyls equivalent.

Clearly the structure of the asymmetric isomer **8a** is related to that of **8b** with attention given to the fact that in this isomer one ruthenium centre contains a hydride ligand *trans* to P^B of the dppm ligand while the other features a hydride *cis* to P^A together with a carbonyl ligand *trans* to this phosphorus donor. The former ruthenium moiety, Ru-P^B, also contains two carbonyl groups *trans* to one another. Based on this data the structure proposed for **8a** is shown below. This structure



8a

also assists us in completing the assignment of the carbonyl resonances attributed to **8a** (Table 3.1). The assignments of CO-1 and CO-2 to Ru-P^B and that of CO-4

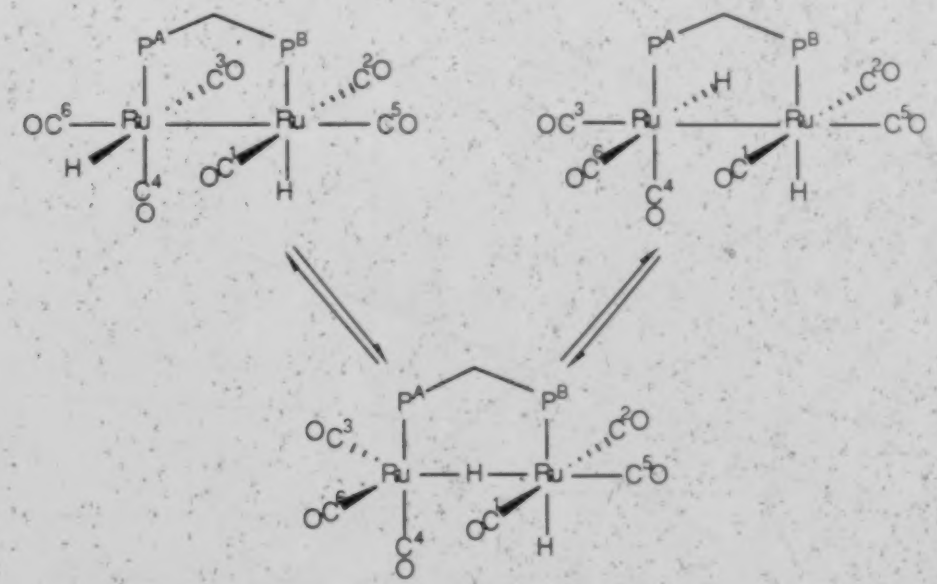
Table 3.1: Carbonyl Resonances in the Near-Limiting ^{13}C n.m.r. Spectrum of Isomer **8a**.

Assignment	δ (p.p.m.)	*J* (Hz)	Integral
1/2	210.2 [dd]	$^2J_{CC} \approx 32$, $^2J_{PC} \approx 7$	1
1/2	208.3 [dd]	$^2J_{CC} \approx 32$, $^2J_{PC} \approx 7$	1
3	204.6 [s]		1
4	202.6 [d]	$J_{PC} = 93.2$	1
5	196.3 [s]		1
6	194.7 [d]	$J_{PC} = 9.2$ Hz	1

and CO-6 to Ru-P^A have been explained before. The high field position of CO-6 is consistent with its position along the Ru-Ru bond which leads to the assignment of the other high field signal at δ 196.3 p.p.m. to CO-5 on Ru-P^B leaving the remaining signal at δ 204.6 p.p.m. assigned CO-3 on Ru-P^A.

The structure proposed for **8a** is consistent with the fluxional behaviour of the carbonyls observed in the variable-temperature ^{13}C n.m.r. spectra at temperatures above 203 K (Scheme 3.2). Coalescence of the singlet ^{13}C resonance at δ 204.6 (CO-3) with the high-field doublet at δ 194.7 p.p.m. (CO-6) is already occurring at temperatures above 223 K. We attribute this coalescence to a migration of the hydride in the plane perpendicular to the diphosphine bridge between the two ruthenium atoms. The two doublets of doublets at δ 210.2 and 208.3 p.p.m.,

Scheme 3.2: Dynamic Behaviour of Isomer **8a**



assigned to CO-1 and CO-2, will also broaden and begin to coalesce at the same rate because movement of the hydride between the two metal centres renders these two carbonyls chemically equivalent. The lone singlet at δ 196.3 p.p.m. remains

relatively sharp up to 258 K because it does not take part in any localized scrambling, and has been assigned to CO-5. At still higher temperatures (not shown in Figure 3.2) the doublet assigned to CO-4 does begin to broaden which may be attributed, in part, to an internal rotation of carbonyls 3,4, and 6 to give a localized scrambling of the $Ru(CO)_3$ moiety.[10] Although onset of isomer interconversion between **8a** and **8b** undoubtedly contributes to carbonyl exchange above this temperature.

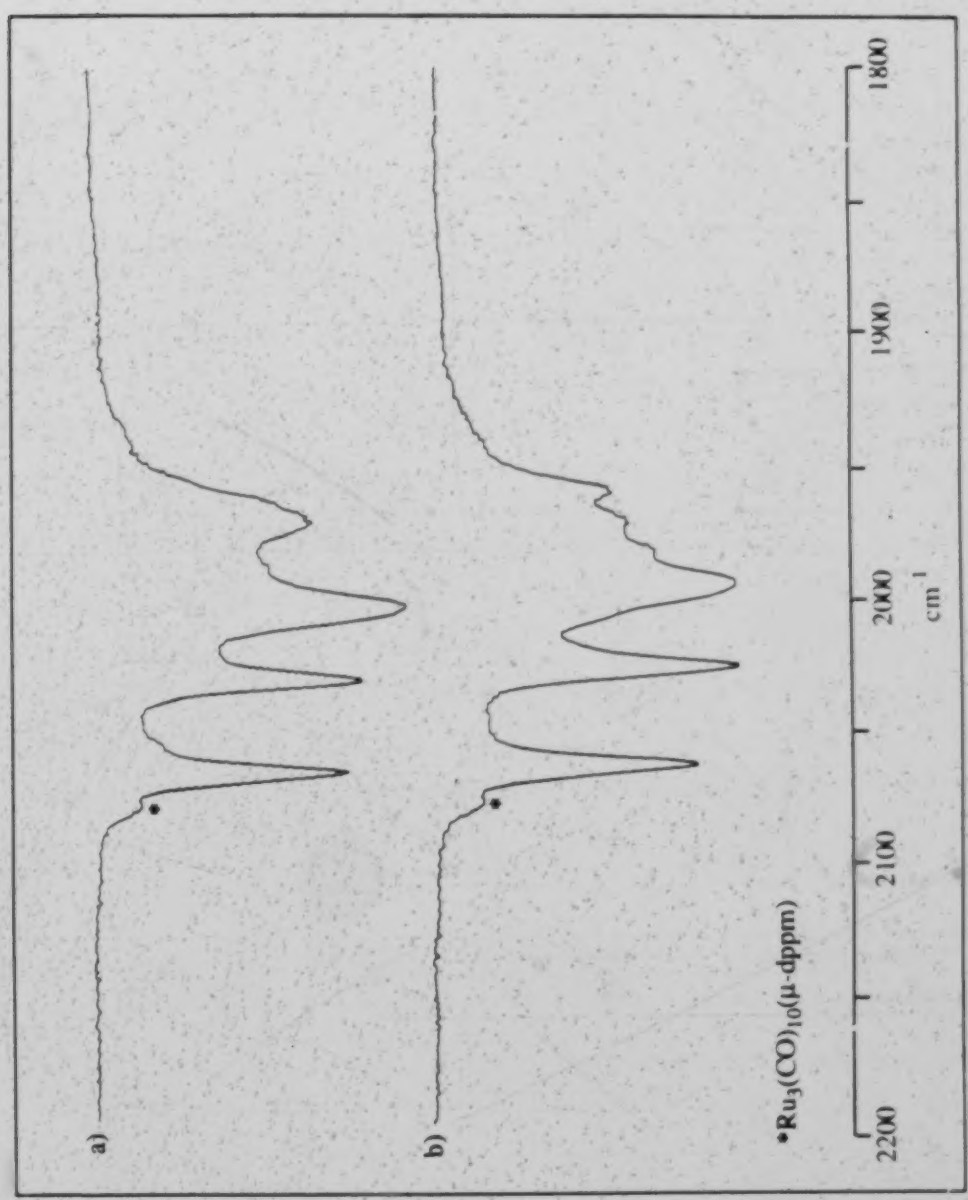
3.2.2. Hydrogen/Deuterium Exchange of 8

Reaction of **8** with D_2 results in a rapid, reversible shift of the carbonyl stretching vibrations from 2065s, 2031s, 2002s, 1987(sh), 1970s,br cm^{-1} to 2064s, 2026s, 1995s, 1984m, 1973m, 1960m cm^{-1} (Figure 3.3). The reversibility of the H/D exchange, and the reactivity of the deutero derivative with CO, respectively, provide clear evidence that simple exchange of H with D has occurred.

Exchange of dihydrogen with dideuterium to produce the dideuteride species was confirmed by ^2H n.m.r. experiments. The ^2H n.m.r. spectrum obtained at 243 K exhibits two broad peaks in the expected high field region. One peak, centred at δ -7.4 p.p.m., is the result of fortuitous overlap of the doublet ^1H resonance at δ -7.28 p.p.m. (**8a**) and the triplet ^1H resonance at δ -7.54 p.p.m. (**8b**). The second peak, centred at δ -8.7 p.p.m., corresponds to the doublets of doublets ^1H resonance at δ -8.80 p.p.m.(**8a**). The chemical shift difference ($\Delta\delta$) between these two peaks is 0.26 p.p.m. from the ^1H n.m.r. spectrum. Considering that the peak width at half-height is nearly 0.5 p.p.m. for the ^2H resonance at δ -8.80 p.p.m. it is

Figure 3.3: Infrared Spectra of **8** in THF, Carbonyl Region:

a) $Ru_2(CO)_6(H)_2(\mu\text{-dppm})$ b) $Ru_2(CO)_6(D)_2(\mu\text{-dppm})$



not surprising that two lower field peaks are found to overlap at δ -7.4 p.p.m.. The broadness of both peaks in the ^{2}H n.m.r. can be attributed, in part, to quadrupolar relaxation.[13] However, the much increased broadening of the ^{2}H signals with respect to the ^{1}H n.m.r. resonances suggests that there may also be exchange broadening. This latter broadening would be due to exchange between isomers **8a** and **8b**. The doublet ^{1}H resonance at δ -7.28 p.p.m. (**8a**) and the triplet ^{1}H resonance at δ -7.54 p.p.m. (**8b**) have a separation of 104 Hz in the 400 MHz ^{1}H n.m.r. spectrum. On going to the 30.7 MHz ^{2}H n.m.r. spectrum the separation has decreased to 8.0 Hz, therefore, for the same slow rate of exchange at 243 K we observe well resolved peaks in the ^{1}H n.m.r. spectrum, but only observe broad peaks in the ^{2}H n.m.r. spectrum. Cooling the sample below 243 K together with broad band ^{31}P-decoupling fails to sharpen the signals in the ^{2}H n.m.r. spectrum. Upon warming the sample to 303 K coalescence of the signals occurs to give a single resonance. This signal appears as the weighted average of the two signals observed at 243 K, appearing at δ -7.8 p.p.m..

Terminal Ru-H stretching vibrations typically occur in the region 2100-1800 cm^{-1}.[14] Often $\nu_{M\text{-}H}$ modes are difficult to detect in the IR spectrum because they usually give rise to weak,[14] and sometimes broad,[15] bands. Also, these bands occur in the carbonyl stretching region and so they may be obscured by the much stronger ν_{CO} bands. Thus it is not always possible to detect the M-H stretching vibration in the IR spectrum. A Ru-H stretching vibration could not be definitely assigned for the ruthenium dihydride complex, **8**.

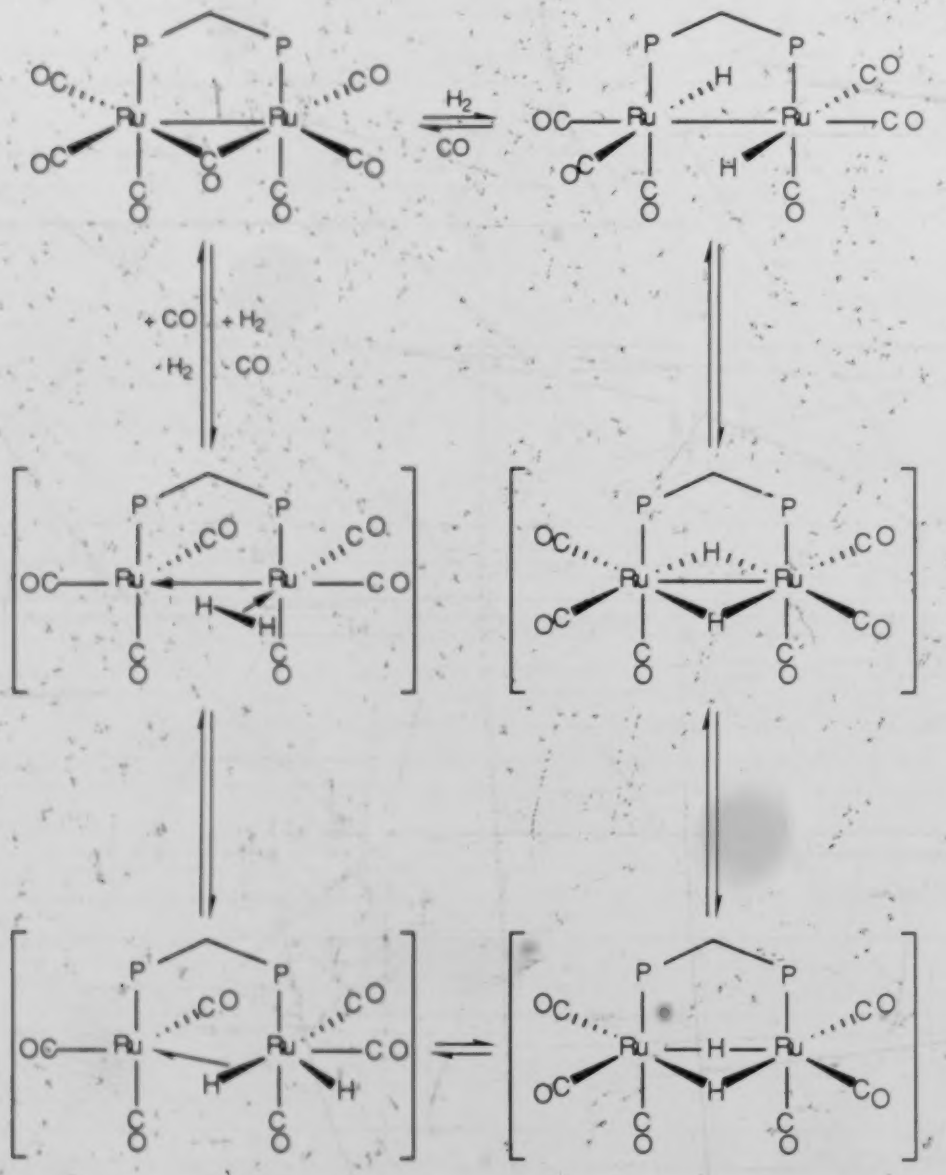
The observed shift in the IR spectrum of the carbonyl resonances may be the result of mixing between the M-H and terminal carbonyl stretching vibrations. The apparent mixing of terminal M-H stretching vibrations with terminal carbonyl stretching vibrations was first reported by Kaesz[16] when it was observed that the ν_{CO} bands of the $Re_3(CO)_{12}H_3$ complex were shifted relative to those in the

deutero derivative $Re_3(CO)_{12}D_3$. Vaska[17] made a similar observation for several monocarbonyl complexes, and determined that mixing of the $\nu_{M\text{-}H}$ and ν_{CO} modes occurs when the hydride is *trans* to the carbonyl ligand. The isotopic shift of the $\nu_{M\text{-}D}$ mode to lower energy diminishes the mixing with the ν_{CO} mode and so a shift in CO stretching vibrations may occur. Further work with hydrido metal complexes containing more than one carbonyl ligand suggested that this mixing, or vibronic coupling, of the carbonyl and hydrido ligands is strongest when these two ligands are mutually *trans* to one another,[18] that is the *trans*-influence results in greater vibronic coupling. There is no requirement stating that all carbonyl bands must shift, indeed one may reasonably expect only those carbonyl ligands in a *trans* or near to *trans* orientation to the hydrido ligands to exhibit vibronic coupling. Thus the apparent shift of some of the IR bands upon addition of D_2 is a reasonable consequence of exchange of hydrogen with deuterium.

Whether oxidative addition of H_2 to $Ru_2(CO)_7(\mu\text{-dppm})$ occurs via an attack at only one metal centre or across both metals simultaneously can only be speculated on. The concerted *cis*-addition of dihydrogen to mononuclear complexes, forming a *cis*-dihydride, have been studied extensively.[19] Reaction of dihydrogen with dinuclear complexes has led to the proposal that H_2 addition to one metal centre, followed by migration of a hydrido ligand to the second metal, is the most probable senario.[19] Unequivocal support (n.m.r. and X-ray) for this mode of attack by H_2 has been given by Vaartstra and Cowie[7b] for the complex $[RhIr(H)_2(CO)_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$. In the case of formation of **8** facile bridge opening, or complete dissociation of the bridging carbonyl ligand will render either ruthenium atom susceptible to attack by H_2. Migration of one hydride to the face opposite the other may occur if the hydrido ligand is able to "tunnel" between the two ruthenium atoms (Scheme 3.3). This "tunneling" process has been proposed by Puddephatt[20] to explain the rearrangement observed in some diplatinum "A"-

frame complexes, and has also been used by Vaartstra and Cowie[7] to explain similar rearrangements in their related complexes.

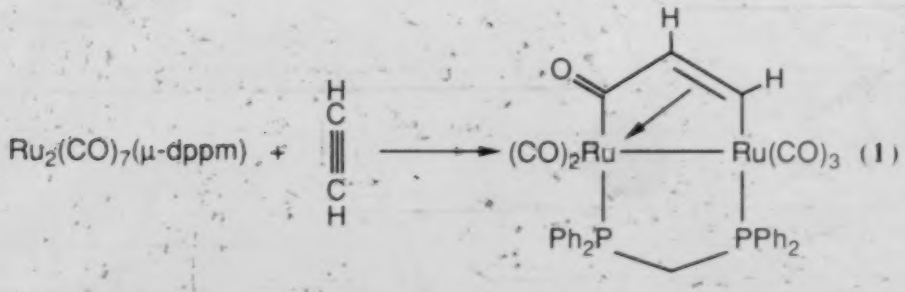
Scheme 3.3: Proposed Mechanism for Hydrogen Migration on Isomer **8b**



3.3. Reactivity of 8

3.3.1. Reaction with Ethyne

A slow purge of ethyne into a THF solution of the dihydride, **8**, results in the formation of a new compound, **9**. The progress of the reaction was monitored by IR spectroscopy which showed loss of carbonyl stretching frequenices due to **8** and the appearance of new bands at 2057s, 1999(sh), 1988vs, 1968s, 1939m, and 1712m cm^{-1}. Comparison of the IR spectrum with that previously reported[21] for the diruthenium cyclopentenone complex (Equation 1) suggested that a relatively smooth reaction of ethyne with the dihydride species had occurred to give the dimetallacyclopentenone compound. The rate of product formation from the dihydride is not as facile as that from $Ru_2(CO)_7(\mu\text{-dppm})$. The latter reaction occurs readily at 0°C and requires an ethyne purge for only a few minutes, while the dihydride reacts at room temperature in approximately fifteen minutes.



(1)

Characterization by ^1H and $^{31}P\{^1H\}$ n.m.r. spectroscopy corroborated the assignment of **9** as the dimetallacyclopentenone derivative. The ^1H n.m.r. spectrum obtained at room temperature showed that there was some contamination of the sample by $Ru_3(CO)_{10}(\mu\text{-dppm})$,[22] an apparently unavoidable consequence of thermal reaction of the labile dihydride species in solution. In addition to a multiplet observed for the hydrogens attached to the phenyl groups, four ^1H n.m.r. signals

were observed for **9**. Two of the four signals are broad, and unresolved indicative of a slow fluxional process (*vide infra*). In order to resolve the two broad signals the sample was cooled to 233 K and the ^{1}H n.m.r. spectrum obtained (Figure 3.4 and Table 3.2). In this spectrum the two signals sharpened and appeared as

Table 3.2: Selected ^{1}H n.m.r. Data for Diruthenium Cyclopentenone Complexes

Compound	^{1}H n.m.r. data δ (p.p.m.) [a]
$Ru_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ **9**	8.22 dd (J_{PH} = 17.2, J_{HH} = 8.5, C*H*CHC[O]) [b] 4.61 dd (J_{PH} = 5.5, J_{HH} = 8.5, CHC*H*C[O]) [b] 4.19 dt (J_{PH} = 14.0, J_{HH} = 11.2, CH_2) 2.79 dt (J_{PH} = 14.0, J_{HH} = 11.2, CH_2)
$Fe_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ [e]	8.63 ddd (J_{PH} = 19, 4, J_{HH} = 7, C*H*CHC[O]) 4.01 q (J_{PH} = 12, CH_2) 3.63 dd (J_{PH} = 2, J_{HH} = 7, CHC*H*[O]) 2.82 dt (J_{PH} = 12, J_{HH} = 10, CH_2)
$Cp_2Ru_2(CO)_2\{\mu\text{-}C_2H_2C(O)\}$ [f]	10.94 d (J_{HH} = 7, C*H*CHC[O]) 3.42 d (J_{HH} = 7, CHC*H*[O]) [c]
$Cp_2Fe_2(CO)_2\{\mu\text{-}C_2H_2C(O)\}$ [f]	12.45 (J_{HH} = 7.5, C*H*CHC[O]) 2.44 (J_{HH} = 7.5, CHC*H*[O]) [d]

[a] Coupling constants reported in Hz
[b] Coupling constants measured at 233 K
[c] Solvent: dichloromethane-d_2
[d] Solvent: chloroform-d
[e] a) Hogarth, G. PhD Thesis, University of Bristol, **1986**, p. 268 b) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc. Chem. Comm.*, **1988**, 358.
[f] Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc. Dalton Trans.*, **1982**, 1297.

doublets of doublets with chemical shifts of δ 8.22 and 4.61 p.p.m.. The low-field shift of one of the signals is characteristic for the shifts observed when a proton is attached to a μ-CH carbene moiety.[23] Earlier work by Knox and co-workers[24] with diiron and diruthenium cyclopentenone derivatives also showed low-field

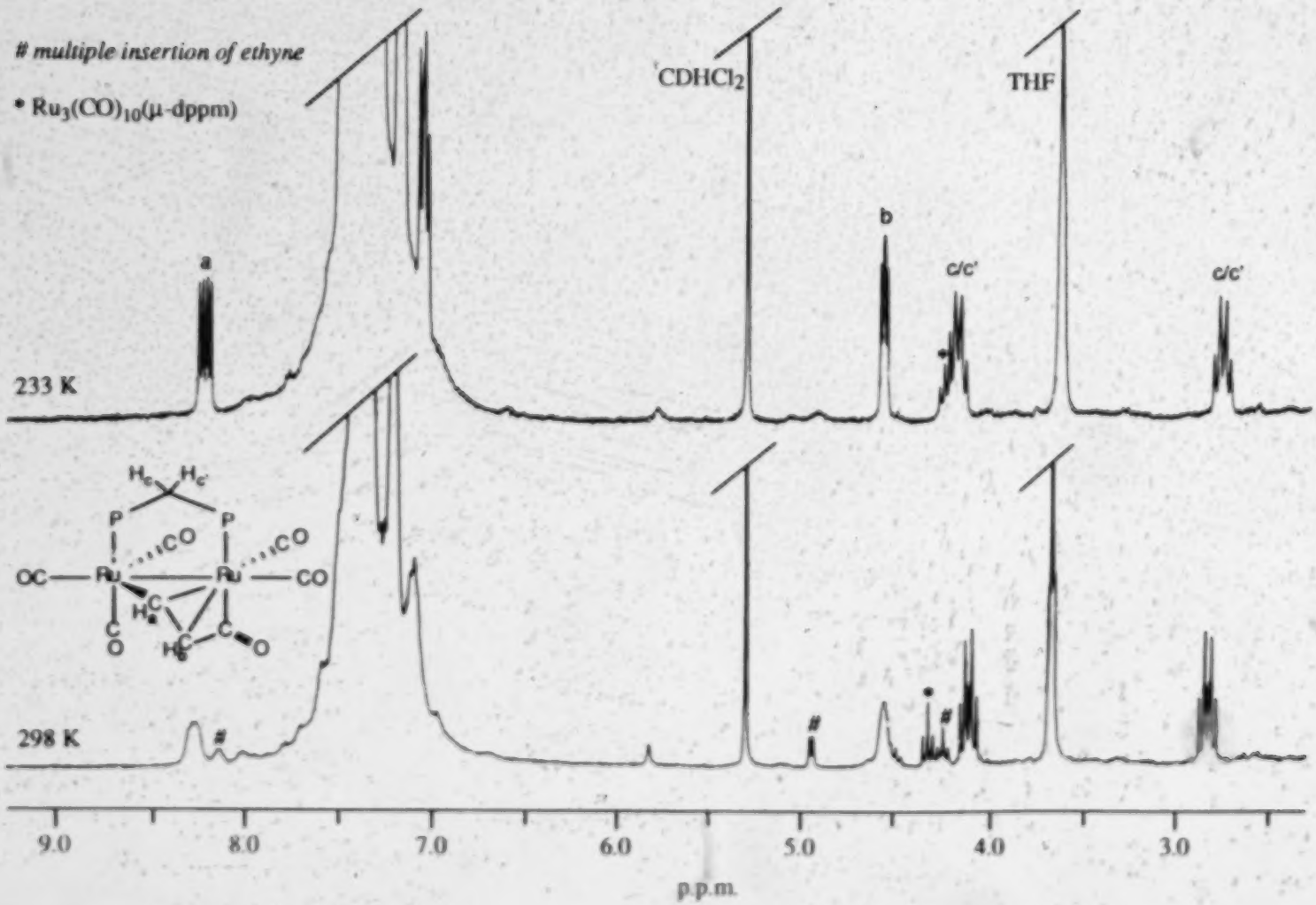
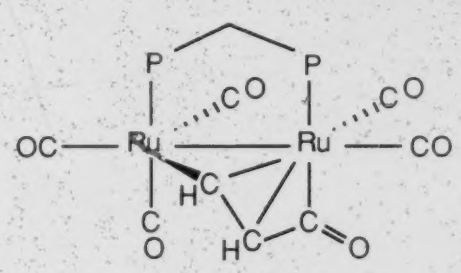


Figure 3.4: Variable Temperature ^1H n.m.r. Spectra of 9

shifts for the proton attached to the carbene-like carbon atom in the μ-CHCHC(O) moiety (Table 3.2). At higher field two other signals are observed, each as a doublets of triplets, and they remain sharp over the temperature range of 233 to 298 K demonstrating that only the alkyne protons are involved in the fluxional process. These signals are assigned to each methylene proton of the bridging dppm ligand. The observed inequivalence of these two protons demonstrate that there is no mirror plane bisecting the metal-diphosphine framework, indicating that the μ-CHCHC(O) moiety must lie to one side of the framework. The molecular structure of the analogous complex $Ru_2(CO)_2[\mu\text{-}C_2Ph_2C(O)](\eta^5\text{-}C_5H_5)_2$ has been determined by X-ray diffraction studies which show the ethylenic bond of the alkyne carbons to be η^2-bound to one ruthenium together with an alkyne-CO link to give the dimetallacyclopentenone complex.[24] In view of the similarities of these complexes we propose **9** to have a similar structure as shown below.

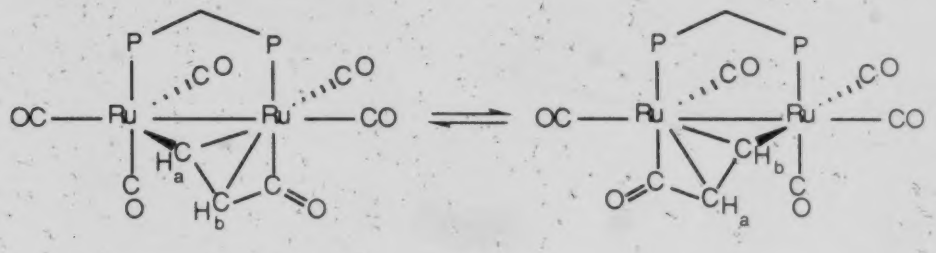


9

In view of the proposed structure the fluxional behaviour exhibited by the ^1H n.m.r. spectra can be accounted for by the process illustrated in Scheme 3.4. In this scheme the breaking of one alkyne-CO link in concert with the formation of a new alkyne-CO link will render the two alkyne protons equivalent,[24] requiring only a minimum of movement from the alkyne moiety. At room temperature the broad, but distinct signals for the alkyne protons indicate that the fluxional motion is still very slow, while at 233 K the motion is completely arrested.

The slowness of the rearrangement is also in accord with the $^{31}P\{^{1}H\}$ n.m.r. spectrum which shows inequivalent phosphorus nuclei as one doublet at δ 44.23 p.p.m. (J_{PP} = 125.8 Hz) and another at δ 30.31 p.p.m. (J_{PP} = 125.8 Hz). These values are identical to those previously reported by our laboratory.[21]

Scheme 3.4: Fluxional Behaviour of **9**

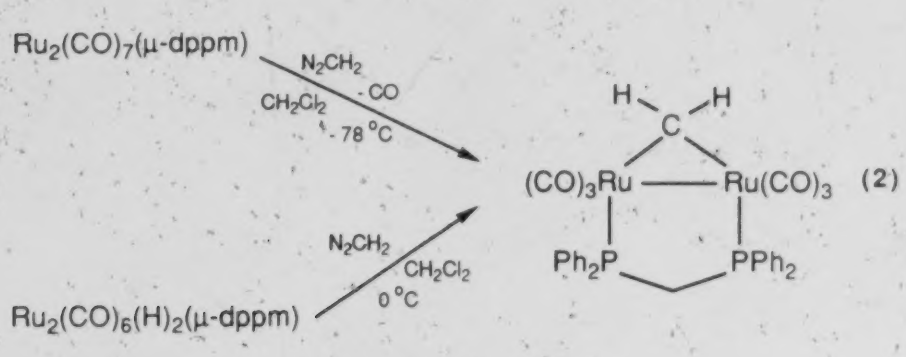


A second minor product is observed in both the ^{1}H and $^{31}P\{^{1}H\}$ n.m.r. spectra, and appears to correspond to the multiple insertion of ethyne. Deliberate attempts to insert another ethyne ligand into the dimetallacyclopentenone unit have been made, and these results will be discussed in the following chapter.

3.3.2. Reaction with Diazomethane

Addition of excess etheral solution of diazomethane to a solution of **8** at room temperature rapidly generates a new compound within two to three minutes as evidenced by changes in the IR spectrum. The IR spectrum showed loss of the bands attributed to **8** and formation of new bands at 2056s, 2019s, 1989m, and 1960s,br cm^{-1} in agreement with those already observed for the known[21] methylene-bridged complex $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$, **10**. No intermediate species could be detected in the IR spectrum. The methylene-bridged complex was originally prepared in our laboratory by reaction of diazomethane with

$Ru_2(CO)_7(\mu\text{-dppm})$ (Equation 2). This latter reaction is extremely facile, and occurs already at -78°C, while the dihydride reacts slowly with diazomethane below 0°C.



The formation of **10** was confirmed by obtaining its ^1H and $^{31}P\{^1H\}$ n.m.r. spectra. All the data agree with those previously reported[21] for this complex. The $^{31}P\{^1H\}$ n.m.r. spectrum consists of a single peak at δ 32.41 p.p.m. indicating that the methylene ligand is symmetrically bridging the two metal centres. The ^1H n.m.r. spectrum displays distinct signals for each proton on the μ-CH_2 ligand and for each proton on the methylene unit of the bridging dppm ligand. Therefore the μ-CH_2 ligand must be adjacent to the metal-diphosphine framework in order to afford each proton a unique environment. Analogous μ-CH_2 containing diruthenium complexes are known[25] (Table 3.3).

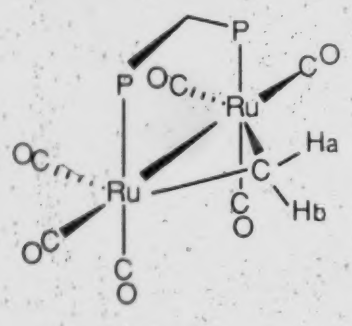
The assignment of the methylene protons of the dppm ligand to the doublets of triplets at δ 3.21 and 3.80 p.p.m. can be made by considering that each proton will show an equal, and large coupling to both phosphorus nuclei. The two μ-CH_2 proton resonances would be expected to be shifted somewhat downfield, a result of the carbene-like character of a single carbon atom that bridges two metal centres.[23] One proton, H_a, will effectively be *syn* to the phosphorus atoms, while the proton H_b will be in an *anti* orientation relative to the phosphorus atoms. Therefore the

Table 3.3: Selected ^{1}H n.m.r. Data for μ-CH_2 Diruthenium Complexes

Compound	^{1}H n.m.r. data δ (p.p.m.) [a]
$Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$ **10**	5.18 dt (J_{PH} = 4.5, J_{HH} = 6.8, μ-CH_2) [b] 4.17 dt (J_{PH} = 15.0, J_{HH} = 6.8, μ-CH_2) 3.80 dt (J_{PH} = 11.0, J_{HH} = 14.0, dppm) 3.21 dt (J_{PH} = 11.0, J_{HH} = 14.0, dppm)
cis-$Cp_2Ru_2(CO)(\mu\text{-}CH_2)(\mu\text{-dppm})$ [d]	8.85 d (J_{HH} = 1.5, μ-CH_2) [c] 5.03 dt (J_{PH} = 15.6, J_{HH} = 1.5, μ-CH_2) 2.26 dt (J_{PH} = 14.6, J_{HH} = 1.5, dppm) 1.35 dt (J_{PH} = 14.6, J_{HH} = 1.5, dppm)
cis-$Cp_2Ru_2(CO)_3(\mu\text{-}CH_2)$ [e]	7.52 s (μ-CH_2) [c] 9.16 s (μ-CH_2)

[a] Coupling constants reported in Hz
[b] Solvent: dichloromethane-d_2
[c] Solvent: chloroform-d
[d] a) Davies, D. L.; Gracey, B. P.; Guerchais, V.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc. Chem. Comm.*, **1984**, 841 b) King, R. B.; Eisch, J. J., Editors, *Organometallic Syntheses*, Elsevier Pub. Co., **1988**, *Volume 4*, p. 217.
[e] Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc. Dalton Trans.*, **1984**, 2293.

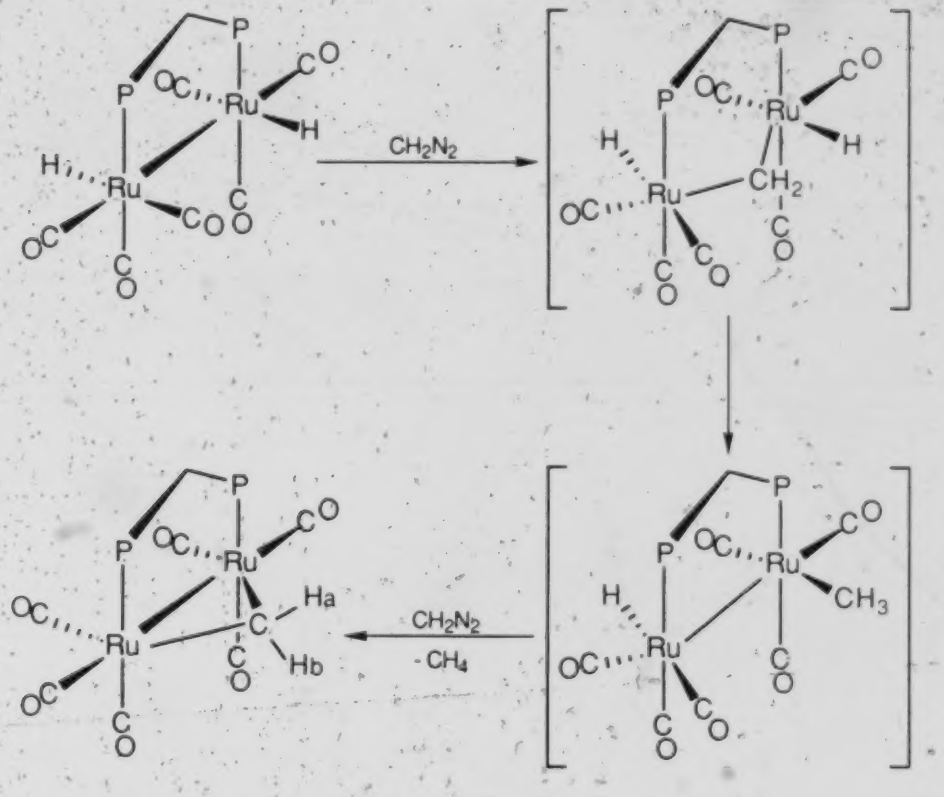
resonance at δ 5.18 p.p.m. is assigned to H_a because it exhibits a small P-H coupling (J_{PH} = 4.5 Hz). Commensurate with this argument the resonance at δ 4.17 p.p.m. is assigned to H_b because it exhibits a much larger P-H coupling (J_{PH} = 15.0 Hz).



10

In a separate experiment in which one equivalent of diazomethane was added to $Ru_2(CO)_6(H)_2(\mu\text{-dppm})$, the IR spectrum showed that the conversion of the dihydride to **10** was incomplete. When the IR spectrum was obtained after addition of excess diazomethane, complete reaction of the dihydride was observed. Analysis of the headspace gases by GC-MS showed that trace amounts of methane was present. No significant amount of H_2 was detected relative to the very small amount of methane present. Although the exact origin of the methane gas can only be speculated on, a reasonable mechanism for its formation can be postulated on the basis of well established organometallic reaction steps. Scheme 3.5 details the

Scheme 3.5: Possible Mechanism for the Reaction of **8** with Diazomethane



proposed process. Insertion of diazomethane into the Ru-Ru bond, followed by CH_2 insertion and reductive-elimination of methane, gives the coordinatively unsaturated diruthenium species which reacts with a second equivalent of diazomethane to produce the observed product **10**.

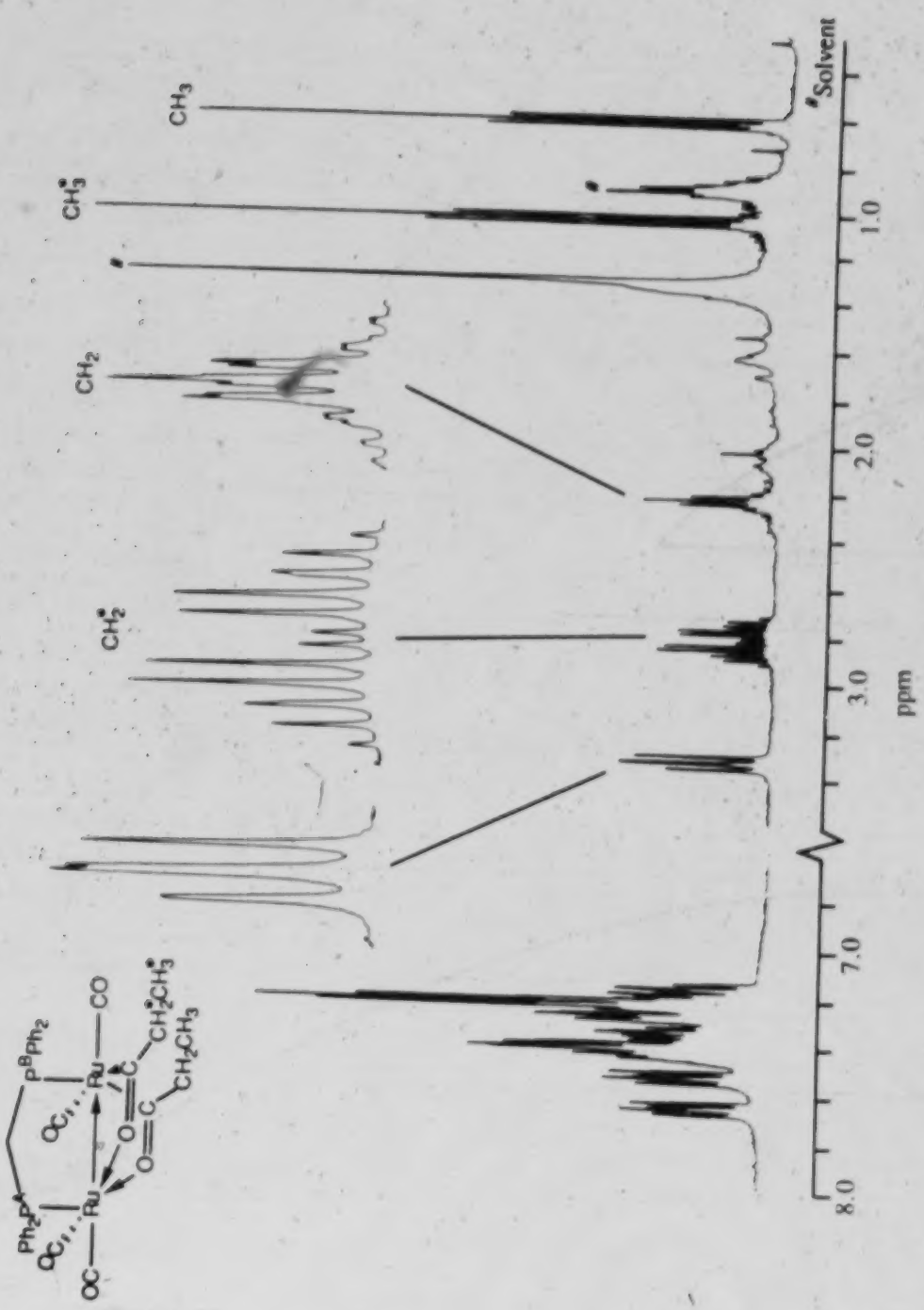
3.3.3. Reaction with Ethylene

Stirring a THF solution of **8** under an atmosphere of ethylene yields a new complex, **11**. Monitoring the reaction by IR spectroscopy in the carbonyl stretching region shows loss of **8** at 2064s, 2031s, 2002s,br, 1970s,br cm^{-1}, and the emergence of **11** at 2003s, 1972s, 1937s, 1918m cm^{-1}. After removal of the solvent the product can be readily extracted into hydrocarbon, from which **11** can be obtained as a yellow, air stable, solid.

The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of **11** show some very interesting features. The $^{31}P\{^1H\}$ n.m.r. spectrum consists of two doublets, one at δ 57.47 p.p.m. (P^A) and the other at δ 37.66 p.p.m. (P^B), (J_{PAPB} = 8[illegible].6 Hz) indicative of two chemically nonequivalent phosphorus nuclei. A doublets of doublets at δ 3.33 p.p.m. in the ^1H n.m.r. spectrum is assigned to the two methylenic protons on the dppm ligand. This signal is attributed to the accidental chemical shift equivalence of the methylene protons. The assignment is based on coupling to the phosphorus nuclei which was shown by selective ^{31}P-decoupled ^1H n.m.r. experiments. Irradiation at P^A caused this signal to collapse to a doublet (J_{PBH} = 9.6 Hz), while irradiation at P^B also resulted in collapse to a doublet (J_{PAH} = 12.0 Hz).

Not including the signals assigned to the dppm ligand there are four other signals in the ^1H n.m.r. spectrum (Figure 3.5). Two of these signals are triplets located in the high field region at δ 1.02 and 0.69 p.p.m., each integrating to three protons relative to the methylene signal of dppm. Neither triplet shows coupling to

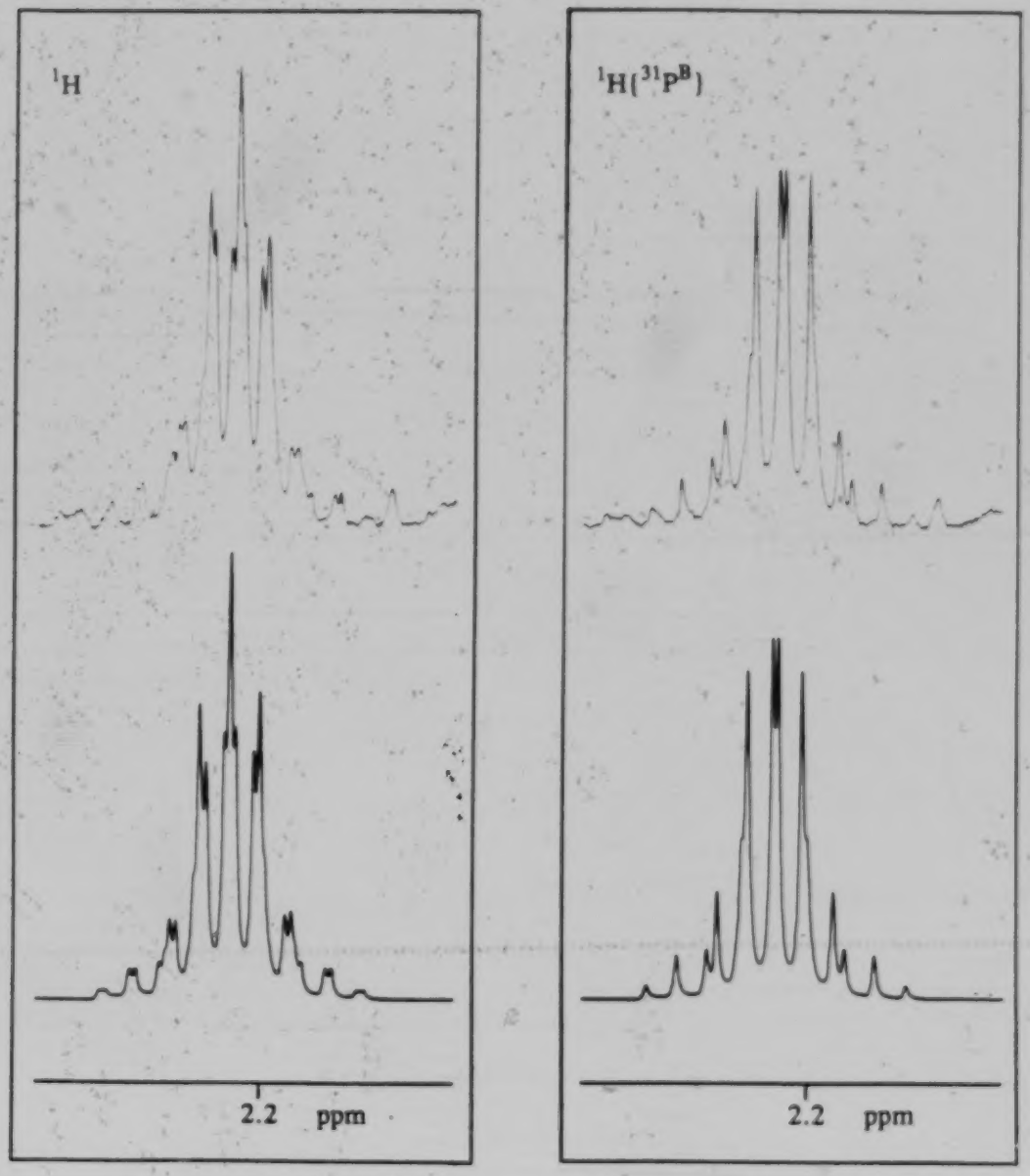
Figure 3.5: ^{1}H n.m.r. Spectrum of **11**



phosphorus but do exhibit H-H coupling indicating that both are methyl groups adjacent to methylenes. The methyl resonance at δ 1.02 p.p.m. has a slightly larger H-H coupling than does its neighbour at δ 0.69 p.p.m., with J_{HH} = 7.4 and 7.2 Hz respectively. The remaining two signals are centred at δ 2.81 and 2.21 p.p.m., and integrate to two protons each as required by the splitting into triplets of the methyl signals. Both methylene signals show complicated splitting patterns. Computer simulation of these signals show that each signal is comprised of two overlapping proton resonances of slightly differing chemical shifts. The patterns exhibited are consistent with diastereotopic methylene protons, that is, the methylene carbon atoms must be chiral. Therefore the signal centred at δ 2.81 p.p.m. is the result of one proton, H_a, at δ 2.86 p.p.m. and the other proton, H_b, at δ 2.76 p.p.m., with both protons exhibiting an ABX_3 spin-system (Table 3.5). Similarily the signal centred at δ 2.21 p.p.m. is comprised of one proton, H_a, at δ 2.23 p.p.m. and the other, H_b, at δ 2.19 p.p.m. with an additional, but small P-H coupling to P^B (J_{PH} = 1.5 Hz) as observed by the loss of this coupling in the $^1H\{^{31}P^B\}$ selectively decoupled n.m.r. spectrum. This higher field methylene group is shown by simulation to be two overlapping ABX_3Y spin systems (Figure 3.6). Selective homonuclear $^1H\{^1H\}$ experiments further corroborated the assignment of these diastereotopic protons to particular carbon atoms. Thus irradiation into the methyl resonance at δ 1.02 p.p.m. resulted in a simplification of the pattern exhibited by both H_a and H_b at δ 2.86 and 2.76 p.p.m. respectively, while irradiation into the methyl resonance at δ 0.69 p.p.m. altered only the signal centred at δ 2.21 p.p.m.

Several ^{13}C n.m.r. experiments were performed to aid in the elucidation of the structure. An attached proton test (APT) ^{13}C n.m.r. was performed with an unenriched sample of **11**. The APT corroborated the ^1H n.m.r. data by confirming the presence of two distinct ethyl groups. Two singlets at δ 9.0 and 8.0 p.p.m. were shown to be methyl groups, while the methylene groups were observed as

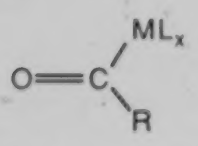
Figure 3.6: Expansion of ^{1}H n.m.r. Signal of **11** Centred at δ 2.19 p.p.m. (*top*) and its Corresponding Computer Simulation (*bottom*)



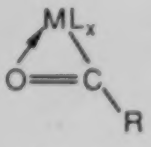
two signals at δ 55.4 and 54.9 p.p.m.. Note that the methylene of the bridging dppm ligand appears as a doublets of doublets at δ 43.6 p.p.m. (J_{PC} = 25.5 and 23.2 Hz).

Reaction of ^{13}CO-enriched **8** with ^{13}C-labeled ethylene was attempted to confirm this assignment by ^{13}C n.m.r. spectroscopy. The ^{13}C n.m.r. spectrum of this sample, measured at 75.4 MHz, clearly shows an intense, broad multiplet at δ 55 p.p.m. as well as intense signals at δ 9.0 and 8.0 p.p.m.. The resonance at δ 9.0 p.p.m. appears as a broad doublet with $^1J_{CC}$ = 33.6 Hz, which is very close to $^1J_{CC}$ of ethane (34.6 Hz) and that observed for $Os_2(CO)_8(\mu\text{-}^{13}C_2H_4)$ (34.0 Hz).[26] The resonance at δ 8.0 p.p.m., a doublets of doublets, exhibits an identical $^1J_{CC}$ of 33.6 Hz together with a smaller coupling of 2.2 Hz.

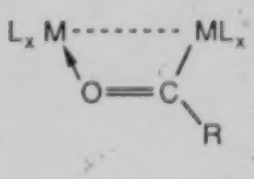
The IR spectrum of **11** in hydrocarbon solvent clearly exhibits an additional weak peak at 1520 cm^{-1}, indicative of a metal-bound acyl moiety,[27] while a ^{13}CO-enriched sample exhibits the same peak shifted to 1484 cm^{-1}. A plethora of metal acyl complexes have been reported in the literature, each illustrating one of the three coordination modes possible for these complexes. The three coordination modes available to an acyl group are: η^1-acyl, which have a single carbon to metal σ-bond; η^2-acyl, which is bonded through both the carbon and the oxygen atoms to the same metal; μ-acyl, which bridges two metal centres with the carbon bound to one metal and the oxygen bound to the other metal. The latter two types function as formal three electron donors.[27] Successful X-ray diffraction studies of some



η^1-acyl



η^2-acyl



μ-acyl

early transition metal complexes unequivocally showed the presence of an η^2-acyl ligand,[28] while the complexes $M_2(CO)_6\{\mu$-O=C[CHC(Ph)NRR']$\}(\mu$-$PPh_2)$ (M = Fe, R = H, R' = Ph; M = Ru, R = R' = Et) were shown to have an acyl ligand bridging the metal centres.[29] Early on, attempts were made to rationalize the differences between η^1- and η^2-acyl bonding based on IR spectroscopy.[27] It has been suggested[30] that the further lowering of the carbonyl stretching frequencies observed for η^2-acyl complexes (1620 - 1450 cm^{-1}) relative to the already low frequencies observed for η^1-acyl complexes (1700-1620 cm^{-1}) may be partially accounted for by considering the potential decrease in C-O bond order available for η^2-bound acyls as a result of the two resonance forms shown below. However, it was also noted that the C-O bond lengths determined by X-ray diffraction studies do not support a lengthening of the C-O bond.[30] More recent work[31] with early

transition metal complexes shows a similar trend in the apparent contradictory nature of the IR (and ^{13}C n.m.r.data, *vide infra*) data of the acyl C-O bond order compared with the results of X-ray diffraction studies.

Acyl complexes of Group 8 transition metals do not always follow the IR trend established by the early transition metal complexes. Several η^1-acyl ruthenium complexes of the type $Ru(CO)_n(X)[\eta^1$-$C(O)Me](PMe_2PH)_{4-n}$ (n = 1, X = Cl, I; n = 2, X = I)[32] do have $\nu_{CO(acyl)}$ (1575- 1595 cm^{-1}) stretching frequencies that are higher than those observed for the complexes $Ru(CO)(Cl)[\eta^2$-$O=C(R)](PPh_3)_2$ (R = Me, $\nu_{CO(acyl)}$ = 1505 cm^{-1}; R = Et, $\nu_{CO(acyl)}$ = 1510 cm^{-1}).[33] However, the related complex, $Ru(CO)(I)[\eta^2$-O=C(Me)$](PPh_3)_2$, clearly goes against this trend with $\nu_{CO(acyl)}$ at 1599 cm^{-1}.[34] Within this broad range established for η^1- and η^2-acyl stretching frequencies (1500 - 1600 cm^{-1}), the

stretching frequencies for μ-acyls may also be found. Several di- and trinuclear ruthenium μ-acyl complexes have been reported[29,35] and all exhibit $\nu_{CO(acyl)}$ stretching frequencies between 1515 and 1550 cm^{-1}.

A more reliable method for the elucidation of the acyl bonding mode may be found in ^{13}C n.m.r. chemical shifts. The use of ^{13}C n.m.r. chemical shifts as a diagnostic tool for carbene complexes is well established.[36,37] The low field resonance of a carbene suggests that substantial deshielding of the carbon is occurring (the carbon is electron deficient). Consistent with this interpretation the ^{13}C n.m.r. chemical shifts observed for the acyl carbon of *mer*-$Ru(CO)(Cl)[\eta^1\text{-}C(O)Me](PMe_2Ph)_3$,[32] and *trans*-$Ru(CO)_2(I)[\eta^1\text{-}C(O)Me](PMe_2Ph)_2$[32] appear at δ 268.5 and 252.8 p.p.m. respectively. An analogous η^2-acyl complex $Ru(CO)(I)[\eta^2\text{-}O{=}C(Me)](PPh_3)_2$ is known,[34] however, no ^{13}C n.m.r. data was reported. The complexes $Ru_2[1,2\text{-}\mu\text{-}O{=}C(Et)][2,1\text{-}\mu\text{-}O{=}C(Et)](CO)_6$,[35b] and $Ru_2[1,2\text{-}\mu\text{-}O{=}C(Et)]_2(CO)_6$[35a] exhibit even lower field ^{13}C n.m.r. shifts at δ 274.8 and 287 p.p.m., respectively, for the μ-O=C(Et) ligand. Complex **11** exhibits two such low field resonances at δ 295.3 and 285.0 p.p.m., very close to those chemical shifts observed for the μ-acyl ligands described above. The ^{13}C n.m.r. data for the ethyl moieties is also in good agreement with the data reported for a μ-O=C(Et) ligand bridging either two ruthenium or two osmium centres.[35]

Additional selective ^{13}C-decoupled ^{13}C n.m.r. experiments were performed with the hope that each methyl signal could be assigned to its corresponding acyl. The decoupling experiments were performed at 50.3 MHz and the accompanying decrease in resolution masked the small coupling of 2.2 Hz observed in the 75.4 MHz n.m.r. spectrum. Irradiation of the lowest field acyl at δ 295.3 p.p.m. caused the methyl signal at δ 8.0 p.p.m. to sharpen, while irradiation at the higher field acyl at δ 285.0 p.p.m. caused the methyl signal at δ 9.0 p.p.m. to sharpen, clearly demonstrating the presence of two distinct "O=C(Et)" moieties. Comparison of the

^{1}H n.m.r. data observed for these two distinct "O=C(Et)" moieties with that reported for the analogous complex Os_3[1,2-μ-O=C(Et)][2,1-μ-O=C(Et)]-$(CO)_{10}$[35b] (Table 3.4) provides additional evidence in support of an ethyl group attached to the acyl carbon.

Table 3.4: Selected ^{1}H n.m.r. Data for the μ-O=C(Et) Ligand

Compound	^{1}H n.m.r. data δ (p.p.m.)[a]	
Ru_2[μ-O=C(Et)]$_2$(CO)$_4$(μ-dppm) **11**	2.81 m[b]	(CH_2, J_{HaHb} = 15.4, J_{HaCH3} = 7.8, J_{HbCH3} = 7.1);
	2.21 m[b,c]	(CH_2, J_{HaHb} = 17.0, J_{HaCH3} = J_{HbCH3} = 7.2)
	1.02 t	(CH_3, J_{HH} = 7.4)
	0.69 t	(CH_3, J_{HH} = 7.2)
Os_3[1,2-μ-O=C(Et)][2,1-μ-O=C(Et)](CO)$_{10}$[d]	2.99 m[b]	(CH_2, J_{HaHb} = 18.5, J_{HaCH3} = J_{HbCH3} = 7.1)
	2.81 m[b]	(CH_2, J_{HaHb} = 18.5, J_{HaCH3} = J_{HbCH3} = 7.1)
	0.96 t	(CH_3)

[a] Coupling constants reported in Hertz.
[b] Centre of ABX_3 spin-coupling pattern.
[c] P-H coupling omitted to clarify comparison, J_{PHa} = J_{PHb} = 1.5 Hz..
[d] Jensen, C. M.; Chen, Y.-J.; Knobler, C. B.; Kaesz, H. D. *New J. Chem.*, **1988**, *12*, 649.

The spectroscopic data for **11** clearly indicates the presence of two acyl groups. In order to maintain an eighteen electron configuration at each ruthenium centre these acyl groups must bind with either a dihapto or a bridging mode. The low field ^{13}C resonances attributed to the acyl groups favours the bridging mode, however, the question as to whether the carbon atoms of both acyls are on one ruthenium or evenly distributed on both metals remains.

The ^{13}C n.m.r. of a ^{13}CO-enriched sample showed six signals in the carbonyl region (Table 3.5). Two of the signals were shifted to low field appearing at δ 285.0 and 295.3 p.p.m., typical of an μ-acyl moiety (*vide supra*). Several selective ^{31}P-decoupled ^{13}C n.m.r. experiments were attempted, however, off-resonance perturbation of the second phosphorus nucleus, caused by the inability to adequately narrow the decoupling bandwidth, rendered the results inconclusive.

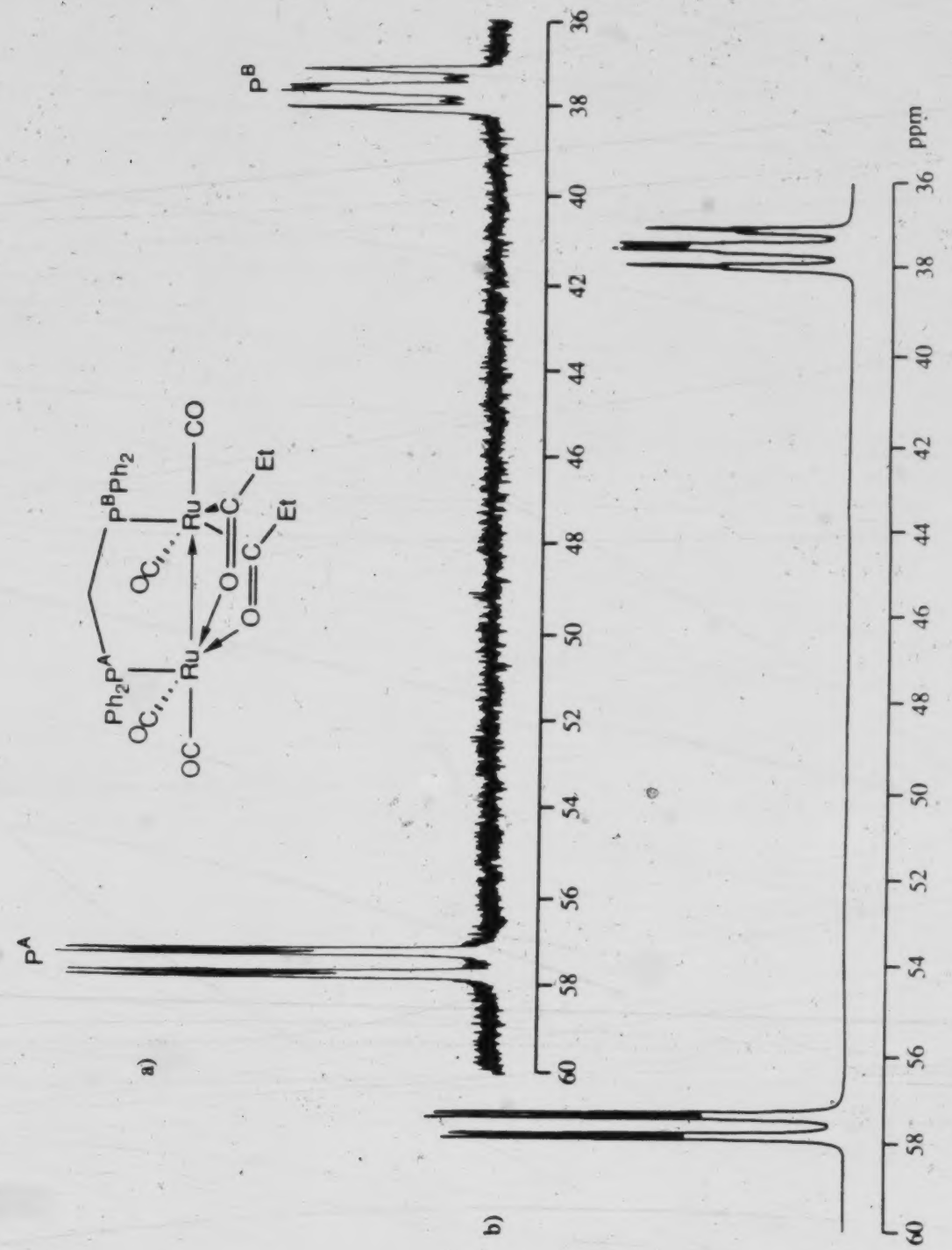
Table 3.5: ^{13}C n.m.r. Data for **11** in the Carbonyl Region

Chemical Shift δ (p.p.m.)	Assignment	Coupling Constant J (Hz)
295.3 dd	$C_a(O)CH_2CH_3$	$J_{PBC} = 9.9$, $J_{CC} = 21.9$
285.0 d	$C_b(O)CH_2CH_3$	$J_{PBC} = 60.9$
212.6 d	CO_c	$J_{PAC} = 17.0$
210.3 dd	CO_d	$J_{PBC} = 10.5$, $J_{CC} = 21.9$
201.0 s	CO_e	
188.0 s	CO_f	

Selective ^{13}C-decoupled ^{13}C n.m.r. experiments were more helpful. Irradiation of the acyl signal at δ 295.3 p.p.m. resulted in a collapse of the doublets of doublets at δ 210.3 p.p.m. to a doublet (J_{CC} = 21.9 Hz). A relatively large C-C coupling has been observed between the η^1-acyl ligand and the carbonyl ligand *trans* to it in the complex $Fe(^{13}CO)_2(Cl)(PMe_3)_2[\eta^1\text{-}^{13}C(O)Me]$[11] ($J_{CCtrans}$ = 15.5 Hz), suggesting that the acyl carbon and one carbonyl are mutually *trans* to one another in **11**.

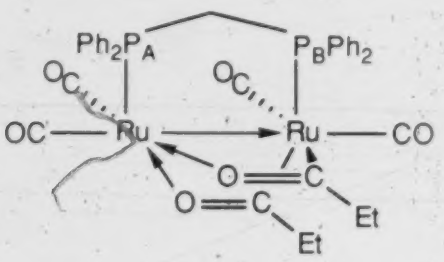
Careful analysis of the $^{31}P\{^1H\}$ n.m.r. spectrum of the ^{13}CO-enriched sample revealed additional information about the structure of **11** (Figure 3.7). The low field ^{31}P resonance, P^A, showed coupling to only one carbon with J_{PAC} = 16.8 Hz, in good agreement with the J_{PAC} of 17 Hz observed for the ^{13}CO resonance at δ 212.6 p.p.m. (Table 3.5). The high field ^{31}P resonance, P^B, gave a

Figure 3.7: a) $^{31}P\{^{1}H\}$ n.m.r. Spectrum of ^{13}CO-enriched **11**
b) Computer Simulated $^{31}P\{^{1}H\}$ n.m.r. spectrum



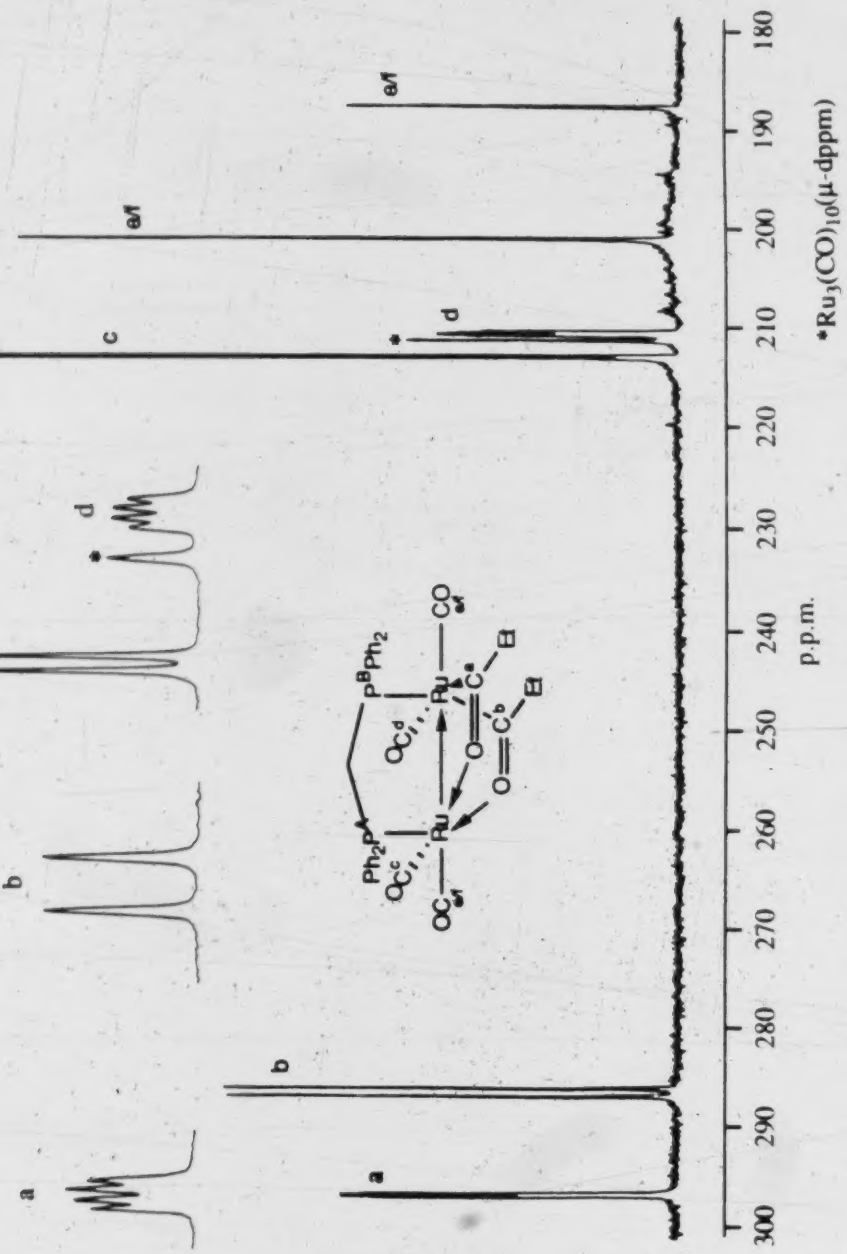
poorly resolved AQXYZ pattern. Together with the large P-P coupling (J_{AQ} = 81.6 Hz), three P-C couplings could be discerned (J_{AX}, J_{AY}, J_{AZ}). The largest P-C coupling, J_{AX} = 60.9 Hz, is similar to the $J_{PCtrans}$ of 82 Hz observed for the complex Ru(CO)(Cl)[η^1-C(O)Me](PPhMe$_2$)$_3$[32] where the η^1-C(O)Me ligand is *trans* to a PPhMe$_2$ group. This corresponds to the J_{PBC} of 60.9 Hz observed for the acyl resonance at δ 285.0 p.p.m.. The remaining two P-C couplings, J_{AY} and J_{AZ}, are nearly identical at approximately 10 Hz each. A J_{PC} of 9.9 and 10.5 Hz is observed for the acyl resonance at δ 295.3 p.p.m. and the carbonyl resonance at δ 210.3 p.p.m. respectively, therefore these resonances are also assigned to the ruthenium atom carrying P^B (Table 3.5 and Figure 3.8).

The remaining two carbonyl resonances (δ 201.0 and 188.0 p.p.m.) appear as singlets. This lack of an observable P-C coupling parallels the behaviour observed for the phosphine-substituted triosmium species, Os(CO)$_{12-n}$(L)$_n$ (n = 1-3, L = PEt$_3$; n = 2-3, L = PMe$_2$Ph).[11a,c] In the limiting ^{13}C n.m.r. spectra of these and other related triosmium species the axial carbonyls *cis* to L show P-C coupling on the order of 6 to 11 Hz, while equatorial carbonyl ligands *cis* to L, and along the Os-Os bond, have no observable P-C coupling.[11] This suggests that the two singlet carbonyl resonances observed for **11** are due to two terminal carbonyls lying along the metal-metal bond. The weight of the accumulated spectroscopic data allows a structural deduction for **11** to be made as illustrated below.

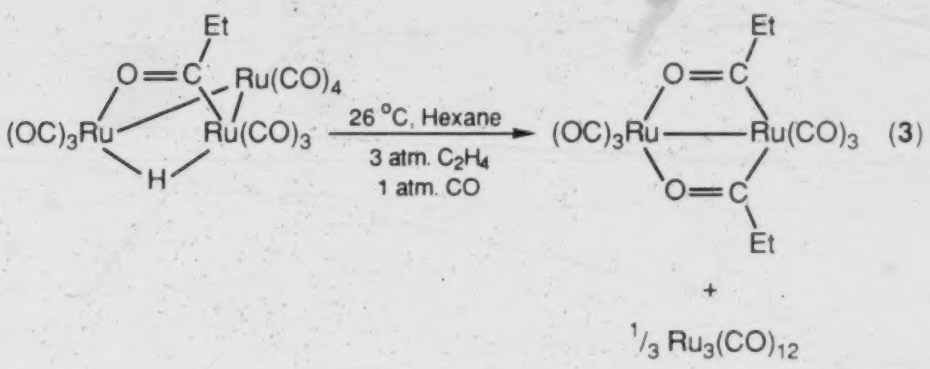


11

Figure 3.8: ^{13}C n.m.r. Spectra of ^{13}CO-Enriched **11**, Carbonyl Region



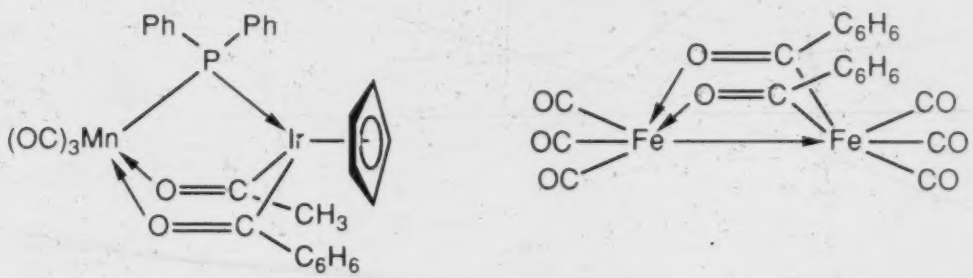
A few examples of bis(μ-acyl) bimetallic complexes can be found in the literature. Indeed, the analogous "pure" carbonyl derivative has been obtained by Kaesz as shown in Equation 3.[38] The molecular structures of two related



(3)

complexes, $Fe_2(CO)_6[1,2\text{-}\mu,\eta^2\text{-}O{=}C(Ph)]_2$[39] and $(OC)_3Mn(\mu\text{-}PPh_2)[1,2\text{-}\mu,\eta^2\text{-}O{=}C(Ph)][1,2\text{-}\mu,\eta^2\text{-}O{=}C(Me)]IrCp$,[40] have been determined by X-ray diffraction studies and the structures redrawn in Figure 3.9. Note that in order to satisfy the eighteen electron rule the diiron complex can be drawn having a metal-metal donor-acceptor bond like that drawn for **11** above.

Figure 3.9: Examples of Donor-Acceptor Bonds with μ-Acyls

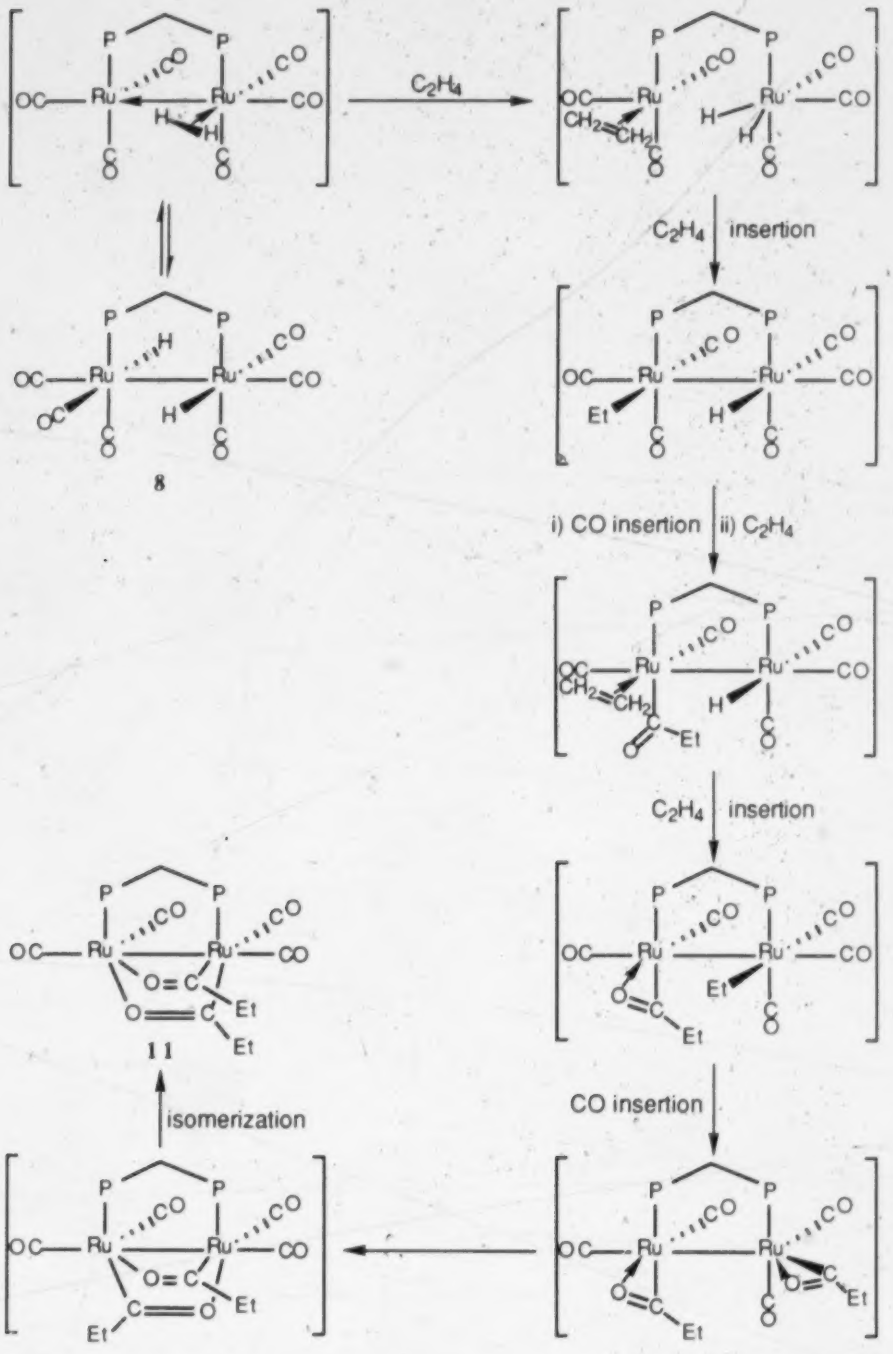


Insertion of a carbonyl into a metal-alkyl bond to form an acyl moiety is well known and has been discussed in a recent review article.[41] More recently direct

evidence for the facile equilibrium between an alkyl and η^2-acyl coordination modes has been published.[42] Therefore it is likely that hydrogenation of coordinated ethylene by the hydride, followed by CO-insertion into the metal-alkyl bond led to the formation of the stable complex **11** as shown in Scheme 3.6. Kaesz and co-workers have shown that $Ru_3(CO)_{10}(\mu\text{-}H)[\mu,\eta^2\text{-}O{=}C(Et)]$ reacts with ethylene and CO to form $Ru_2(CO)_6[1,2\text{-}\mu\text{-}O{=}C(Et)]_2$ and $Ru_3(CO)_{12}$ (Equation 3, *vide supra*).[38] Presumably the formation of the diruthenium species goes via a hydride/CO insertion mechanism similar to that proposed in Scheme 3.6.

The isomerization depicted in the final step of Scheme 3.6 is similar to that observed by Kaesz[35b] for the isomerization of $Os_3[1,2\text{-}\mu\text{-}O{=}C(Et)][2,1\text{-}\mu\text{-}O{=}C(Et)](CO)_{10}$ to $Os_3[1,2\text{-}\mu\text{-}O{=}C(Et)]_2(CO)_{10}$ at room temperature in benzene solution. Kaesz notes that no isomerization is observed for the dinuclear complex $Ru_2(CO)_6[1,2\text{-}\mu\text{-}O{=}C(Et)]_2$.[35b] He speculates that this lack of isomerization may be the result of a very strong interaction between the bridging acyl groups and the metal atoms, which is reflected in a very short Ru-Ru bond (2.686(1) Å). The other isomeric form of the diruthenium complex, $Ru_2(CO)_6[1,2\text{-}\mu\text{-}O{=}C(Et)][2,1\text{-}\mu\text{-}O{=}C(Et)]$ can be prepared by the oxidation of $\{Ru_3[\mu\text{-}O{=}C(Et)]_2(\mu\text{-}CO)_2(CO)_8\}^{2-}$ with $[Me_3O][SbCl_6]$.[35b] Triruthenium dodecacarbonyl is formed as a side product (31%). Again, no isomerization is observed for this complex. The dimerization of $\{Fe(CO)_4[\eta^1\text{-}C(O)R]\}^-$ (R = Ph or Me)[39] does not form a mixture of isomers, instead it exclusively favours the formation of $Fe_2[1,2\text{-}\mu\text{-}O{=}C(R)]_2(CO)_6$. In light of the very few known examples of bis(μ-acyl) dinuclear carbonyl complexes it is difficult to predict whether or not isomerization of the acyl groups will occur, and so the possibility cannot be ruled out.[43]

Scheme 3.6: Proposed Route to the Formation of **11**



3.4. Experimental Section

3.4.1. Starting Materials and Reagents

$Ru_2(CO)_7(\mu\text{-dppm})$, **2**, was prepared by method a) as outlined in Chapter Two. Diazomethane was generated as an etheral solution from 1-methyl-3-nitro-1-nitrosoguanidine (MNNG), which was purchased from Aldrich Chemical Company and used as received. Dihydrogen (U.H.P.) and acetylene were obtained from Union Carbide Inc. (Canada), while ^{13}C-enriched carbon monoxide (99.1%) and ethylene (99.0%) were purchased from Isotec (Matheson) Inc. and Icon Isotope Services, respectively.

3.4.2. Synthetic Procedures

Preparation of $Ru_2(CO)_6(H_2)(\mu\text{-dppm})$, 8

$Ru_2(CO)_7(\mu\text{-dppm})$, **2**, (48 mg, 0.0613 mmole) was dissolved in freshly distilled THF (7 ml) under an argon atmosphere. The solution was transferred under argon to a small three-neck round bottom flask (25 ml) fitted with a gas inlet and a Dry Ice condenser. Dihydrogen was slowly passed through the solution via a #22 gauge needle while stirring the solution at room temperature in the dark. The reaction was monitored by IR spectroscopy until all **2** was consumed, (ca. 45 minutes), forming $Ru_2(CO)_6(H)_2(\mu\text{-dppm})$ which has ν_{CO} bands at 2064s, 2031s, 2002s,br, 1970s,br cm^{-1}. The lability of the hydrides has prevented successful isolation of **8** as a solid, even at low temperature (-78°C), consequently it has been characterized in solution.

IR (THF, ν_{CO}): 2064s, 2031s, 2002s,br, 1970s,br cm^{-1}.

^1H n.m.r. (THF-d_8, 233 K): **8a**, δ 7.2-7.7 (m, phenyl), 4.22 (t, 2H, CH_2, J_{PH} = 10 Hz), -7.28 (d, 1H, Ru-H, J_{PHcis} = 23.2 Hz), -8.80 (dd, 1H, Ru-H, $J_{PHtrans}$ = 72, $^4J_{PH}$ = 14.8 Hz); **8b**, δ 7.2-7.7 (m, phenyl), 4.61 (t, 2H, CH_2, J_{PH} = 10 Hz), -7.54 (t, 2H, Ru-H, $^2J_{PH} + {}^4J_{PH}$ = 10.4 Hz).

$^{31}P\{^1H\}$ n.m.r. (THF-d_8, 233 K): **8a**, δ 38.9 (d, P^A, J_{PAPB} = 97.8 Hz), 25.8 (d, P^B, J_{PBPA}= 97.8 Hz); **8b**, δ 30.0 (s).

$^{13}C\{^1H\}$ n.m.r. (THF-d_8, 203 K): **8a**, δ 210.2 (dd, 1CO, $^2J_{CC} \approx 32$, $^2J_{PC} \approx 7$ Hz), 208.3 (dd, 1CO, $^2J_{CC} \approx 32$, $^2J_{PC} \approx 7$ Hz), 204.6 (s, 1CO), 202.6 (d, 1CO, $J_{PACtrans}$ = 93.2 Hz), 196.3 (s, 1CO), 194.7 (d, 1CO, J_{PAC} = 9.2 Hz), 129-133 (m, phenyl); **8b**, δ 204.6 (d, 2CO, $J_{PCtrans}$ = 91.4 Hz), 199.3 (s, broad, 4CO), 129-133 (m, phenyl).

Deuterium Exchange with 8

The hydrogenation product, **8**, was generated as described above. Once conversion to **8** was complete the dihydrogen purge was stopped and the atmosphere above the solution gently purged with argon. Dideuterium was then passed through the solution, in the same way as dihydrogen, for 10 minutes, at which point the IR spectrum indicated that exchange had occurred with a slight shift in the carbonyl stretching frequencies to 2064s, 2026s, 1995s, 1973m, 1960m cm^{-1}. Purging the solution for another 15 minutes did not result in any further changes in the IR spectrum.

IR (THF, ν_{CO}): 2064s, 2026s, 1995s, 1973m, 1960m cm^{-1}.

^2H n.m.r. (THF, 243 K): δ -7.4 (br), -8.7 (br).

Preparation of Diazomethane

An Erlenmeyer flask (25 ml) was charged with a Teflon coated magnetic stir bar, 50% (w/w) KOH solution (2.5 ml), and diethyl ether (7 ml). The mixture is cooled in an ice bath to 0°C and, with gentle stirring, MNNG was slowly added (245.6 mg, 1.67 mmole) over approximately 25 minutes. A pale yellow etheral solution of diazomethane resulted. The ether layer was decanted into another Erlenmeyer flask containing dry KOH pellets, the flask stoppered, and cooled in a freezer for a minimum of two hours. If the pellets were fused together after this time the solution was decanted into another flask containing fresh KOH pellets and the solution cooled in the freezer for two more hours before use. Yield: 37%

The yield was determined[44] by reacting the etheral diazomethane solution with an excess of benzoic acid (424.6 mg, 3.48 mmole) and then back-titrating the unreacted benzoic acid with a 0.099 M KOH solution, using phenolphthalein as indicator.

Reaction of 8 with Ethyne: Preparation of $Ru_2(CO)_5[\mu\text{-}CHCHC(O)](\mu\text{-}dppm)$, 9

$Ru_2(CO)_7(\mu\text{-}dppm)$, **2**, (50 mg, 0.0639 mmole) was dissolved in freshly distilled THF (10 ml) under an argon atmosphere. The solution was transferred under argon to a small three-neck round bottom flask (25 ml) fitted with a gas inlet and a Dry Ice condenser. Dihydrogen was slowly passed through the solution via a #22 gauge needle and the solution stirred at room temperature in the dark. The reaction was monitored by IR spectroscopy until all **2** was consumed, (ca. 45 minutes), forming $Ru_2(CO)_6(H)_2(\mu\text{-}dppm)$ which has ν_{CO} bands at 2064s, 2031s, 2002s,br, 1970s,br cm^{-1}. The dihydrogen purge was stopped, and ethyne was

then passed through the solution in the same manner. The acetone stabilizer present in the ethyne was removed by first passing the ethyne through a Dry Ice/acetone-cooled cold trap. Complete reaction was confirmed when the IR spectrum showed new ν_{CO} bands at 2057s, 1996(sh), 1989vs, 1968s, 1939m, 1714w cm^{-1}, and complete comsumption of the dihydride. The solvent was removed *in vacuo* at 0°C to yield a red-brown residue. The residue was dissolved in dichloromethane (ca. 1-2 ml) and pentane added until a precipitate formed. The mixture was then cooled to -78°C for one hour. The precipitated product was recovered by filtering off the solution and then drying the precipitate *in vacuo* at room temperature. The resulting light yellow-brown powder, **9**, was washed successively with three, two millilitre portions or pentane, and was finally dried *in vacuo* at room temperature. Yield 64.2%.

IR (THF, ν_{CO}): 2057s, 1999(sh), 1988vs, 1968s, 1939m, 1712m cm^{-1}.

^1H n.m.r. (CD_2Cl_2, 233 K): δ 8.22 (dd, 1H, C*H*CHC[O], J_{PH} = 17.2, J_{HH} = 8.5 Hz), 7.3-7.7 (m, 20H, phenyl), 4.61 (dd, 1H, CHC*H*C[O], J_{PH} = 5.5, J_{HH} = 8.5 Hz), 4.19 (dt, 1H, CH_2, J_{PH} = 14.0, J_{HH} = 11.2 Hz), 2.79 (dt, 1H, CH_2, J_{PH} = 14.0, J_{HH} = 11.2 Hz).

$^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 44.23 (d, J_{PP} = 125.8), 30.31 (d, J_{PP} = 125.8).

Reaction of 8 with Diazomethane: Preparation of $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-}dppm)$, 10

The dihydride, **8**, was prepared from **2** (52 mg, 0.066 mmole) in freshly distilled diethyl ether (10 ml). Excess diazomethane was added as an etheral solution (5 ml, 0.4 mmole) to the THF solution of **8**, and the combined solutions were stirred in the dark at room temperature. After several minutes stirring the IR

spectrum of the solution was obtained and showed complete loss of the ν_{CO} bands due to **8** and new ν_{CO} bands at 2052s, 2012s, 1975s,br cm^{-1}. The solvent was removed *in vacuo* at 0°C to yield a deep red-brown residue. The residue was washed successively with three, two millilitre portions of pentane and was then dried *in vacuo* at room temperature to give **10** as a brown solid. Yield 51.3%.

IR (THF, ν_{CO}): 2056s, 2019s, 1989m, 1960s,br cm^{-1}.

^1H n.m.r. (CD_2Cl_2, 298 K): δ 7.3-7.7 (m, 20H, phenyl), 5.18 (dt, 1H, μ-CH_2, J_{PH} = 4.5, J_{HH} = 6.8 Hz), 4.17 (dt, 1H, μ-CH_2, J_{PH} = 15.0, J_{HH} = 6.8 Hz), 3.80 (dt, 1H, CH_2, J_{PH} = 11.0, J_{HH} = 14.0 Hz), 3.21 (dt, 1H, CH_2, J_{PH} = 11.0, J_{HH} = 14.0 Hz).

$^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 32.41 (s).

Reaction of 8 with Ethylene: Preparation of $Ru_2(CO)_4[\mu,\eta^2\text{-}O{=}C(CH_2CH_3)]_2(\mu\text{-dppm})$, 11

The dihydride, **8**, was prepared from **2** (50 mg, 0.0639 mmole) in freshly distilled THF (12 ml). Once the formation of **8** was complete the dihydrogen purge was stopped and the solution frozen. The flask was evacuated and one atmosphere of ethylene admitted while allowing the solution to slowly warm to room temperature. The solution was stirred in the dark for one and a half hours. The solution was frozen a second time, the flask evacuated, and another atmosphere of ethylene admitted. The solution was stirred under the ethylene atmosphere, in the dark, until the IR spectrum showed complete conversion to the new product with ν_{CO} bands at 2003s, 1972s, 1937s, 1918m and 1520w cm^{-1}. The solvent was removed *in vacuo* at 0°C to yield a red residue. The product was extracted into two, twenty millilitre portions of pentane, filtered, and the solvent removed *in*

vacuo at 0ºC. The resulting yellow solid was dried *in vacuo* at room temperature to give **11** in 42% yield.

IR (THF, ν_{CO}): 2003s, 1972s, 1937s, 1918m, 1520w cm^{-1}.

^1H n.m.r. (CD_2Cl_2, 298 K): δ 6.4-8.1 (m, 20H, phenyl), 3.33 (dd, 2H, PCH_2P, J_{PAH} = 9.6, J_{PBH} = 12.0), 2.81 (AQX_3Y, 2H, CH_2, J_{HaHb} = 15.4, J_{HaCH3} = 7.8, J_{HbCH3} = 7.1, J_{HaPB} = J_{HbPB} = 1.5 Hz), 2.21 (ABX_3, CH_2, J_{HaHb} = 17.0, J_{HaCH3} = J_{HbCH3} = 7.2 Hz), 1.02 (t, CH_3, J_{HH} ≈ 7.4 Hz), 0.69 (t, CH_3, J_{HH} ≈ 7.2 Hz).

$^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 57.45 (d, P^A, J_{PP} = 81.6 Hz), 37.66 (d, P^B, J_{PP} = 81.6 Hz).

$^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 295.3 (dd, *C*[O]Et, J_{PBC} = 9.9, J_{CC} = 21.9 Hz), 285.0 (d, *C*[O]Et, J_{PBC} = 60.9 Hz), 212.6 (d, CO, J_{PAC} = 17.0 Hz), 210.3 (dd, CO, J_{PBC} = 10.5, J_{CC} = 21.9 Hz), 201.0 (s, CO), 188.0 (s, CO), 55.4 (s, CH_2), 54.9 (dd, CH_2, J_{PC} = 12, $J_{P'C}$ = 10), 43.6 (dd, PCH_2P, J_{PC} = 25.5 $J_{P'C}$ = 23.2 Hz), 9.0 (s, CH_3), 8.0 (s, CH_3).

Preparation of ^{13}CO-Enriched
$Ru_2(CO)_4[\mu,\eta^2\text{-}O{=}C(CH_2CH_3)]_2(\mu\text{-dppm})$, 11

$Ru_2(CO)_7(\mu$-dppm) (50 mg,0.0639 mmole) was dissolved in freshly distilled THF (12 ml) under an argon atmosphere. The solution was transferred under argon to a small three-neck round bottom flask (50 ml) fitted with a gas inlet. The solution was frozen, the flask evacuated, and then one atmosphere of ^{13}CO admitted while allowing the solution to slowly warm to room temperature. The solution was stirred in the dark under ^{13}CO for one to two hours. The IR spectrum was obtained and showed the characteristic shift of the well resolved ν_{CO} bands at 2054 and 1751 cm^{-1} to 2007 and 1716 cm^{-1} respectively. The solution was frozen

a second time, the flask evacuated, and one atmosphere of argon admitted. The solution was allowed to warm to room temperature and the flask fitted with a Dry Ice condenser. Dihydrogen was slowly passed through the solution via a #22 gauge needle while the solution was stirred in the dark. The reaction was monitored by IR spectroscopy until all ^{13}CO-enriched **2** was consumed (ca. 45 minutes), and $Ru_2(^{13}CO)_6(H)_2(\mu\text{-dppm})$ is produced, (ν_{CO} 2018s, 1984s, 1962s, 1928s cm^{-1}). The dihydrogen purge was stopped and the solution frozen. The flask was evacuated and one atmosphere of ethylene (or ^{13}C-enriched ethylene) admitted while allowing the solution to slowly warm to room temperature. The solution was stirred in the dark for one hour. The solution was then frozen a fourth time, the flask evacuated, and one atmosphere of ethylene admitted. The solution was stirred for a second time under an atmosphere of ethylene (or ^{13}C-enriched ethylene), in the dark, until the IR spectrum showed complete conversion to the new product with ν_{CO} bands at 1956s, 1928s, 1912m, 1892s, 1876m, 1484w cm^{-1}. The solvent was removed *in vacuo* at 0°C to yield a red residue. The product was extracted into two, twenty millilitre portions of pentane, filtered, and the solvent removed invacuo at 0°C. The resulting yellow solid was dried *in vacuo* at room temperature to **11** in 28% yield.

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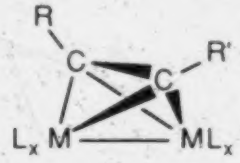
Chapter Four

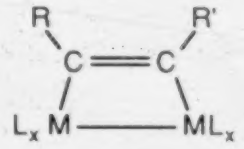
Reactions of $Ru_2(CO)_7(\mu\text{-dppm})$ With Alkynes

4.1. Introduction

Generation of dimetallacycles by the reaction of bimetallic transition metal carbonyls with alkynes has been the subject of considerable study in the past.[1] In these complexes the alkyne bridging the metal centres has been observed to adopt one of two bonding modes -- the $\mu\text{-}\eta^1{:}\eta^{1'}$ ("parallel") mode or the $\mu\text{-}\eta^2{:}\eta^{2'}$ ("perpendicular") mode, and examples of these two modes have been obtained in X-ray crystallographic investigations.[1e,f]



$\mu\text{-}\eta^2{:}\eta^{2'}$ mode



$\mu\text{-}\eta^1{:}\eta^{1'}$ mode

Insertion of a carbonyl into one of the alkyne-metal bonds to generate another set of dimetallacycle, the dimetallacyclopentenone, has also been reported.[2] The isolation of this type of dimetallacycle suggests that it may be representative of the intermediates involved in the first step toward the catalytic formation of organic molecules from alkynes and CO, mediated by transition metal complexes (see Scheme 1.5). The isolation of metal-bound lactones,[3] quinones,[4] and cyclopentadienones[5] via the reaction of metal carbonyls with alkynes lends further support to this hypothesis.

The utility of iron carbonyls in organic synthesis[6,7] and in furnishing glimpses of probable intermediates as stable complexes[7] is well known. However,

the majority of the chemistry of ruthenium carbonyls with alkynes is limited to trinuclear species.[8] It is of interest, therefore, to develop and study the reactivity of alkynes with the diruthenium carbonyl derivative $Ru_2(CO)_7(\mu\text{-dppm})$.

4.2. Synthesis and Characterization of Compounds

4.2.1. Reaction of 2 with Ethyne

A slow purge of ethyne into a dichloromethane solution of $Ru_2(CO)_7(\mu\text{-dppm})$, **2**, at 0°C rapidly forms a new species. The IR spectra obtained during the course of the reaction clearly show a smooth conversion to the product. Of note is the loss of the band at 1751 cm^{-1} due to the bridging carbonyl of **2**, and the appearance of a new band at 1712 cm^{-1}, which is typical for a ketonic carbonyl.[2a] A similar overall change in the IR spectrum is observed for the photochemical reaction of the analogous diiron complex, $Fe_2(CO)_7(\mu\text{-dppm})$, with ethyne to form $Fe_2(CO)_5[\mu\text{-}C(O)C_2H_2](\mu\text{-dppm})$.[2b] To illustrate the similarities between the diiron complex and the new product a comparison of the carbonyl stretching frequencies is presented in Table 4.1. From this comparison it appears that the reaction of **2** with ethyne leads to the formation of the analogous dimetallacyclopentenone complex, $Ru_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$, **9**.

The extreme facility of the reaction of **2** with ethyne becomes clear when one compares the reaction conditions of the diiron and the diruthenium complexes. The diruthenium complex, **2**, readily loses a carbonyl ligand and adds one ethyne unit at 0°C, in the absence of light, while the analogous diiron complex of Knox must be irradiated for one hour (500 watt lamp in a silica vessel) while purging with ethyne to complete the conversion to the dimetallacyclopentenone complex.[2b]

Similarily, reaction of the dimetallic cyclopentadienyl derivatives, $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (M = Fe, Ru), with an alkyne requires, at best, several hours of ultraviolet irradiation to afford the cyclopentenone product.[2a] The molecular structure of the

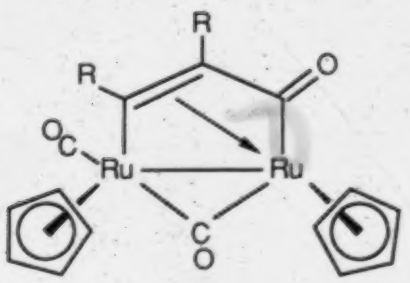
Table 4.1: Comparison of IR Spectral Data for Reaction of $M_2(CO)_7(\mu\text{-dppm})$ (M = Fe, Ru) with Ethyne [a]

M	$M_2(CO)_7(\mu\text{-dppm})$	$M_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$
Fe	2045s, 1992s, 1978s, 1941s, 1922(sh), 1755m [b]	2043m, 1975s, 1960(sh), 1923w,1725w [c]
Ru	2059s, 2014s, 1992s, 1957s 1937m, 1748m [d]	2057s, 1996(sh), 1989vs, 1968s, 1939m, 1714w [d]

[a] Solvent: Dichloromethane
[b] Hogarth, G. *PhD Thesis*, University of Bristol, **1986**, p. 233.
[c] Hogarth, G.; Kayser, F; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc. Chem. Comm.*, **1988**, 358.
[d] a) Kiel, G.-Y.; Takats, J. *Organometallics*, **1989**, *8*, 839 b) This work.

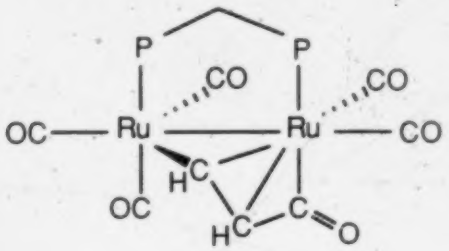
diphenylacetylene derivative, $Ru_2(CO)_2[\mu\text{-}C_2Ph_2C(O)](\eta^5\text{-}C_5H_5)_2$, was confirmed by an X-ray diffraction study.[2a] It was found that the bonding in the dimetallacyclopentenone may be formally represented as having the ethylenic moiety η^2-bound to the same ruthenium to which the ketonic carbonyl is attached.

The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of **9** have already been discussed in detail in Chapter 3, Section 3.3.1., and appear in the literature,[9] so only a review of the salient features are presented here. Consistent with the formalism for a dimetallacyclopentenone species, two signals for the μ-CHCHC(O) ligand appear in the ^1H n.m.r. spectrum, with one proton resonance significantly shifted to low field. Two doublets of triplets, assigned to each proton on the methylene unit of the dppm ligand, together with the observation of two doublets in the $^{31}P\{^1H\}$ n.m.r.



R = Ph

spectrum, demonstrate that the two phosphorus atoms are inequivalent. Based on this spectroscopic data, and the similarities of **9** with the analogous complexes $Ru_2(CO)_2[\mu\text{-}C_2Ph_2C(O)](\eta^5\text{-}C_5H_5)_2$[2a] and $Fe_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$,[2b] the molecular structure of **9** is proposed below.



9

4.2.2. Reaction of 2 with Dimethylacetylene Dicarboxylate

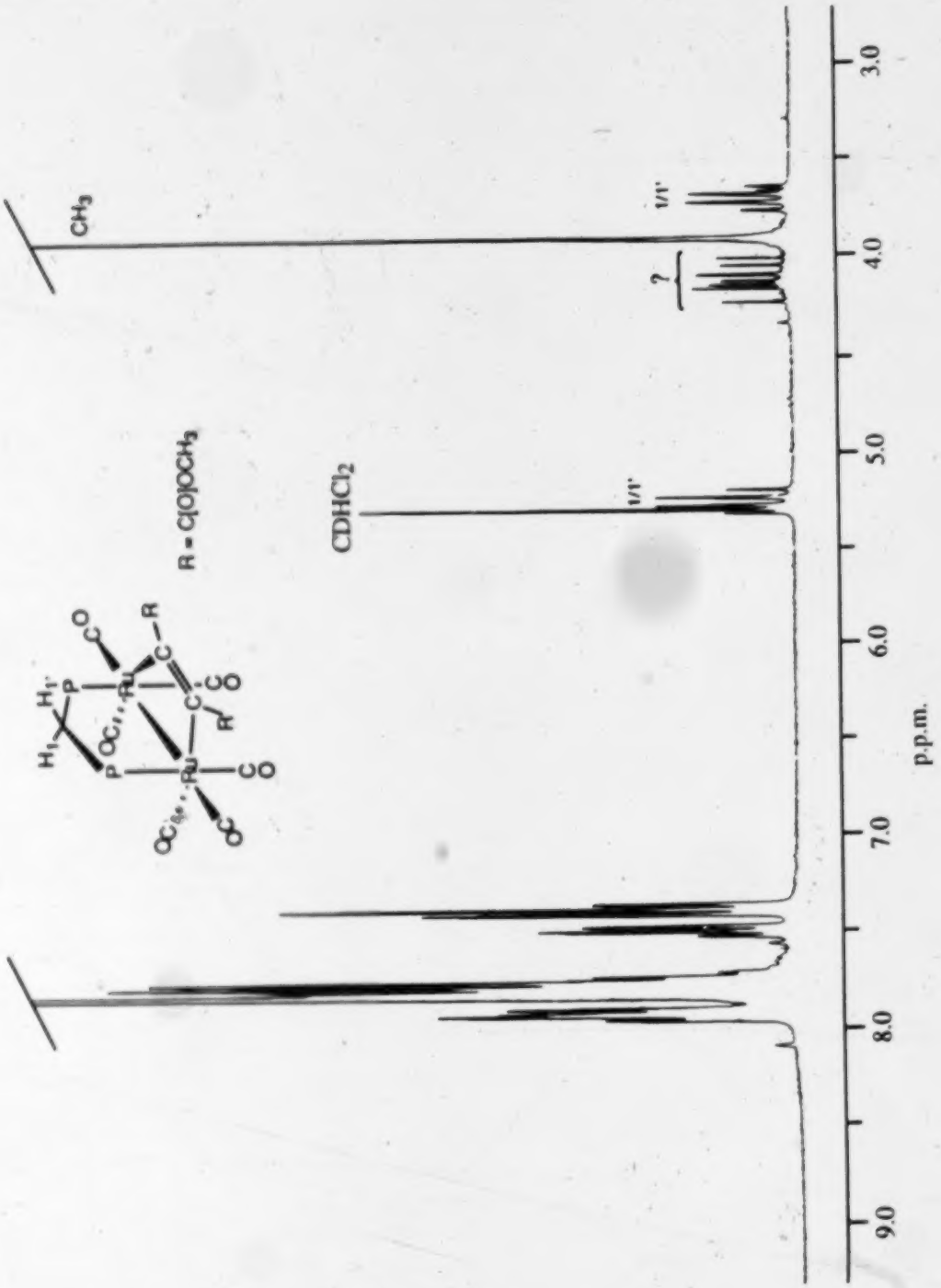
The thermal reaction of $Ru_2(CO)_7(\mu\text{-dppm})$, **2**, with the activated alkyne dimethylacetylene dicarboxylate, (dmad), occurs readily at room temperature. The IR spectrum taken one hour after addition of dmad to a THF solution of **2** showed that consumption of **2** was complete and that a new product, **12**, had formed with carbonyl stretching frequencies at 2070s, 2034s, 2006m, 1986s, 1965(sh), 1709vw, 1692w cm^{-1}. The weak stretches at 1709 and 1692 cm^{-1} may be

attributed, at least in part, to the carboxyl groups of dmad, which is in contrast with the strong ν_{CO} stretching frequency of free ligand at 1731 cm^{-1} (THF). Some decomposition to the well known, thermally stable trinuclear species $Ru_3(CO)_{10}(\mu$-dppm) also occurs.

The $^{31}P\{^1H\}$ n.m.r. spectrum of the compound exhibits one resonance at δ 20.3 p.p.m.. In the ^1H n.m.r. spectrum of a sample dissolved in CD_2Cl_2, the two methylene protons on the dppm ligand are assigned to a pair of doublets of triplets at δ 4.56 and 3.33 p.p.m. respectively (J_{PH} = 11, J_{HH} = 13.4 Hz). The methyl groups of dmad appear as one singlet at δ 3.31 p.p.m., integrating to six protons relative to each signal attributed to the methylene protons. As a result of the overlap of the methyl resonance with one of the methylene resonances the ^1H n.m.r. of the sample was obtained in a mixed solvent of CD_2Cl_2/C_6D_6 (2:3). This ^1H n.m.r. is shown in Figure 4.1 where the methylene resonances are now at δ 5.29 and 3.72 p.p.m., and the methyl resonance appears at δ 3.95 p.p.m.. The chemical equivalence of the two phosphorus nuclei and of both methyl groups in the ^{31}P n.m.r. and ^1H n.m.r. spectra, respectively, show that the dmad ligand is symmetrically bridging the two metals. The inequivalence of the methylene protons in the ^1H n.m.r. spectrum indicate that the dmad ligand must be normal to the plane containing the diruthenium-diphosphine framework.

The ^{13}C n.m.r. spectrum for the μ-η^1:$\eta^{1'}$-$C_2(CO_2CH_3)_2$ ligand of **12** is very similar to that observed for the analogous complex $Cp_2Ru_2(CO)_2(\mu$-$CO)[\mu$-η^1:$\eta^{1'}$-$C_2(CO_2CH_3)_2]$ reported by Knox and co-workers[2a] (Table 4.2). However, the alkyne carbons bound to ruthenium could not be detected in the ^{13}C n.m.r. spectrum of **12** . The dominant spin lattice relaxation mechanism for ^{13}C is from dipole-dipole interaction with protons directly attached to the ^{13}C atom, and so this lack of a ^{13}C resonance for an unenriched, quarternary carbon atom is not entirely unexpected because non-protonated carbon atoms tend to have much longer

Figure 4.1: ^{1}H n.m.r. Spectrum of **12** in Mixed Solvent CD_2Cl_2: C_6D_6 (2:3, v/v)



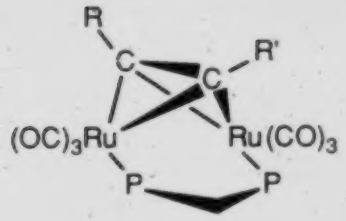
relaxation times than protonated carbons.[10]

Table 4.2: ^{13}C Chemical Shifts for $Ru_2[\mu\text{-}\eta^1\text{:}\eta^{1'}\text{-}C_2(CO_2CH_3)_2]$ Moieties

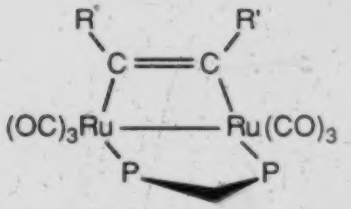
Complex	δ ^{13}C (p.p.m.) [a]		
	$C_2CO_2CH_3$	$C_2CO_2CH_3$	$C_2CO_2CH_3$
$Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^{1'}\text{-}C_2(CO_2CH_3)_2](\mu\text{-dppm})$ **12**	51.2	–	171.6
$Cp_2Ru_2(CO)_3[\mu\text{-}\eta^1\text{:}\eta^{1'}\text{-}C_2(CO_2CH_3)_2]$ [b]	52.1	122.4	170.1

[a] Solvent: dichloromethane-d_2
[b] Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc. Dalton Trans.*, **1982**, 1297.

Even though the bonding mode of the alkyne cannot be determined by making a direct comparison of the ^{13}C chemical shifts for the alkyne carbon atoms there is still sufficient information to derive the correct structure of **12**. There are two possible orientations of the alkyne carbon-carbon bond relative to the metal-metal bond. One possible orientation of the alkyne unit is normal to the metal-metal bond, in a $\mu\text{-}\eta^2\text{:}\eta^{2'}$ bonding mode, which would be sterically unfavourable (structure **A**). With this orientation the methoxy carboxylate groups, R and R', are in different environments which is clearly not observed in the ^{13}C (Table 4.2) and the ^1H n.m.r. spectra. Note also the lack of a metal-metal bond in order to satisfy the eighteen electron rule. The second orientation would place the alkyne unit parallel to the metal-metal bond to give a dimetallacyclobutene type complex with a $\mu\text{-}\eta^1\text{:}\eta^{1'}$ bonding mode (structure **B**). This latter orientation satisfies both the ^{13}C and the ^1H n.m.r. data because it places both methyl carbons and both carboxylate carbons in the same chemical environment and renders H_1 and $H_{1'}$ distinct. This



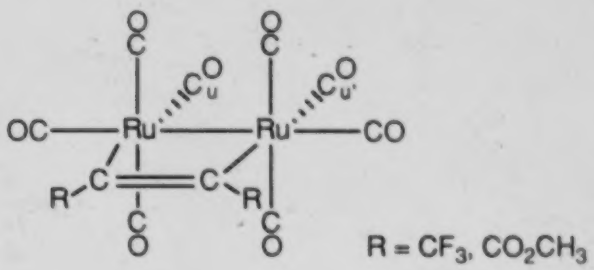
(A)



(B)

coordination mode differs from that observed for $Ru_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-}dppm)$, **9**, where insertion of a carbonyl ligand into a metal-alkyne bond occurred to generate the dimetallacyclopentenone species. From the work by Knox and co-workers it appears that electron deficient alkynes, or "activated" alkynes, often adopt a simple bridging position.[2a] A few examples when activated alkynes do undergo CO insertion to form a dimetallacyclopentenone species have been reported for dimethylacetylene dicarboxylate $Cp_2M_2(CO)_n[\mu\text{-}C_2(CO_2Me)_2C(O)]$ (M = Fe,[2a] n = 2; M = W,[2c] n = 4), and diphenylacetylene $Cp_2M_2(CO)_2[\mu\text{-}C_2(Ph)_2C(O)]$ (M = Fe, Ru).[2a]

To confirm these results the ^{13}C n.m.r. spectrum of ^{13}CO-enriched **12** was obtained. The ^{13}C n.m.r. spectrum exhibits three, equal intensity signals in the carbonyl region. Two resonances appear as doublets at δ 203.1 and 191.8 p.p.m., with both resonances having the same, small coupling to phosphorus, $J_{PC} \approx 5$ Hz (Figure 4.2). These two carbonyl resonances can be tentatively assigned based on the assignments made for the related complexes $Ru_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^{1'}\text{-}C_2R_2)$ (R = CF_3,[11a] CO_2CH_3[11b]). In these compounds two unique carbonyl ligands, CO_u and $CO_{u'}$, can be unambiguously assigned from the variable temperature ^{13}C n.m.r. spectra of these complexes because they do not scramble, whereas the six remaining carbonyl ligands lie in the same plane and undergo a facile site exchange via the well-known "merry-go-round" process.[12] The limiting ^{13}C n.m.r. spectra

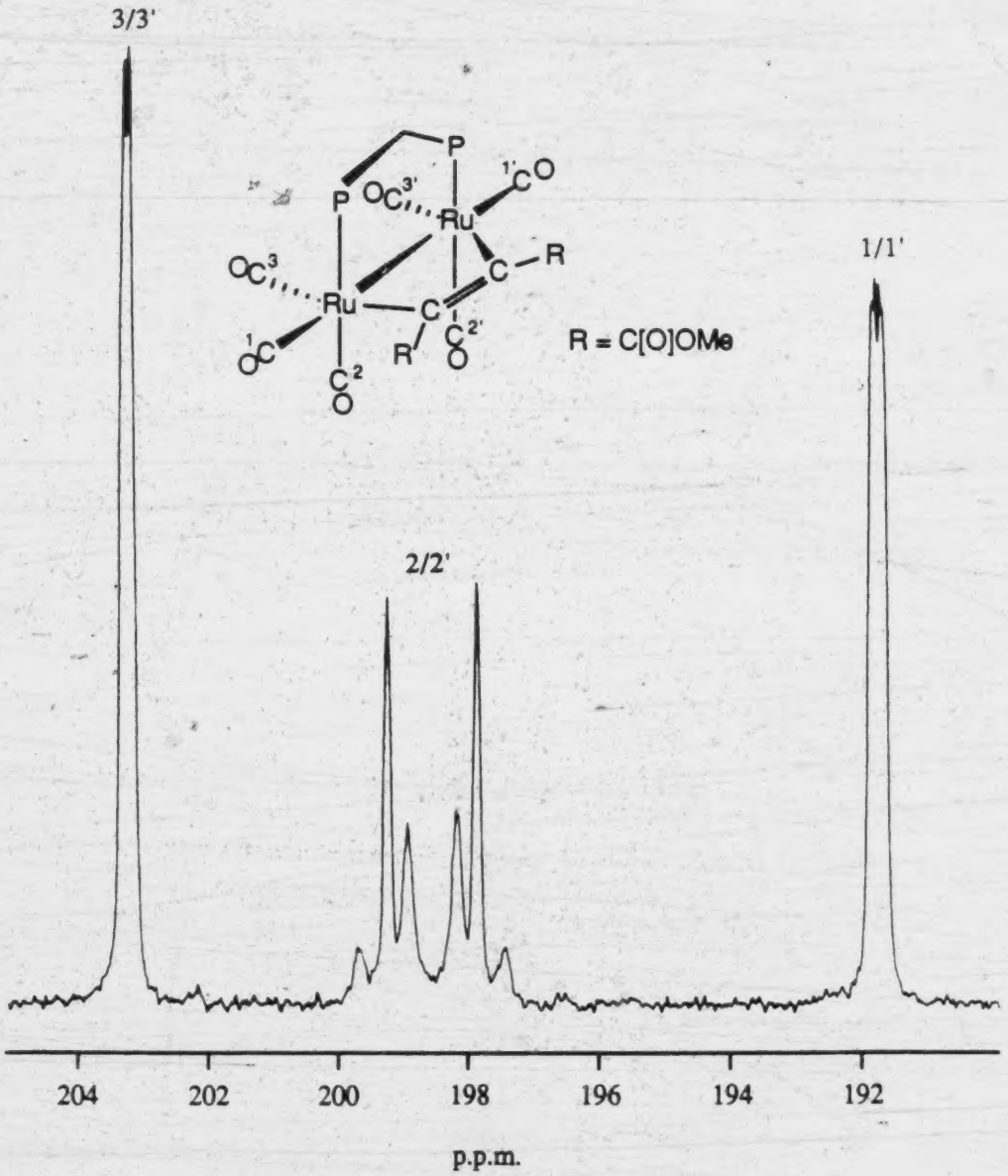


were also obtained and, in each case, the carbonyl ligand *trans* to the bridging alkyne ligand resonates at lower field than the two carbonyl ligands lying along the M-M bond axis. Therefore, the doublet observed in the ^{13}C n.m.r. spectrum of **12** at δ 203.1 p.p.m. may be tentatively assigned to the two carbonyl ligands *trans* to the bridging dmad ligand, while the doublet at δ 191.8 p.p.m. would then correspond to the two carbonyl ligands that lie along the Ru-Ru bond axis.

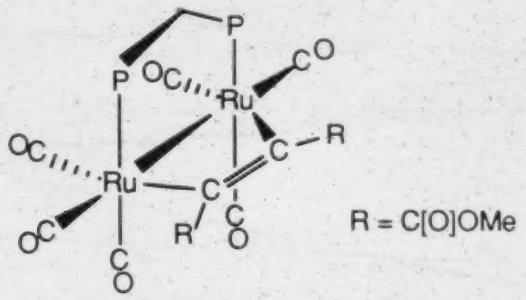
The third resonance that is observed in the ^{13}C n.m.r spectrum of **12**, at δ 198.6 p.p.m., exhibits a second-order AA'XX' spin system (Figure 4.2). The signal was simulated[13] and the coupling constants determined: $J_{PC} = 99.5$, $J_{P'C} = 2.5$, $J_{PP'} = 56.0$ Hz.

The *trans* P-C coupling found for a variety of dirhenium carbonyl complexes that contain a single, bridging dppm ligand have been reported to range from 47 to 74 hertz.[14] However, slight changes in the coordination mode of the other ligands to the rhenium metal centres can have a marked affect on the magnitude of $J_{PCtrans}$.[14b] In this light the calculated value of 99.5 hertz for the *trans* P-C coupling for complex **12** does not seem so unusual although it is somewhat large. The $J_{PP'}$ observed for the heterodimetallacyclopentenone complexes $(OC)_2Fe(\mu\text{-dppm})[\mu\text{-}C(O)C_2R_2]Pt(PPh_3)$[15] may serve as a rough guide of the magnitude of the P-P coupling when dppm bridges two metal centres. For a number of alkynes used in these complexes the value of $J_{PP'}$ remains relatively unchanged ranging from 51 to 61 hertz. The P-P coupling calculated from the

Figure 4.2: ^{13}C n.m.r. Spectra of ^{13}CO-Enriched **12**, Carbonyl Region



AA'XX' pattern observed in the ^{13}C n.m.r. spectrum of **12** falls in the middle of this range at 56 hertz. Thus there is little doubt that the structure of **12** is as shown below.



12

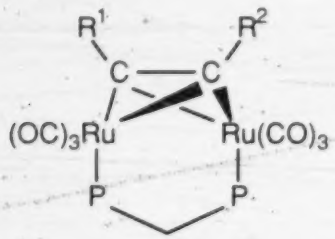
4.2.3. Reaction of 2 with Diphenylacetylene

Stirring a THF solution of $Ru_2(CO)_7(\mu$-dppm), **2**, in the presence of excess diphenylacetylene, at 52°C for several hours results in the formation of a new product **13**. The reaction was monitored by IR spectroscopy which clearly shows consumption of starting material, **2**, and formation of **13** with bands at 2023m, 1990s, 1967m cm^{-1}. Some decomposition to the well known, thermally stable trinuclear species $Ru_3(CO)_{10}(\mu$-dppm) also occurs. The majority of trinuclear contaminant can be separated from the product by chromatography on a florisil column. However, decomposition on the column results in a significant reduction in the isolated yield.

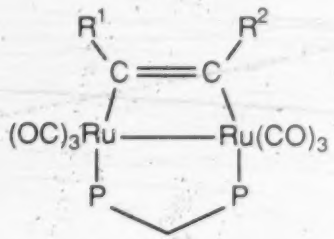
The product, **13**, has been fully characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ n.m.r. spectroscopy. A singlet at δ 37.4 p.p.m. in the ^{31}P n.m.r. is assigned to **13**. The ^1H n.m.r. spectrum exhibits a triplet at δ 3.53 p.p.m. (J_{PH} = 9.5 Hz), attributed to the methylene group of the dppm ligand, and a multiplet spanning the range of δ 6.8 to 7.5 p.p.m.. The relative integration of these signals

show that one diphenylacetylene ligand is coordinated to the metal centres because the multiplet integrates to thirty protons relative to the methylene resonance, corresponding to four phenyl groups of the dppm and two of the diphenylacetylene ligands.

In order for the methylene protons to be chemically equivalent, the diphenylacetylene ligand must be coordinated *trans* to the dppm ligand, thereby giving the complex a mirror plane containing the two phosphorus atoms and bisecting the methylene protons of the bridging dppm ligand. There are two possible orientations for an alkyne symmetrically bridging two metal centres: one gives a "tetrahedrane" core, where the carbon-carbon bond is positioned normal to the metal-metal bond (**C**) in a μ-η^2:$\eta^{2'}$ bonding mode; the other gives a dimetallacyclobutene core, where the carbon-carbon bond is oriented such that it is colinear with the metal-metal bond (**D**) in a μ-η^1:$\eta^{1'}$ bonding mode.



(C)



(D)

The differences in the bonding modes and the attendant changes in hybridization of the alkyne carbons in structures **C** and **D** should be reflected in the ^{13}C chemical shifts of these carbon atoms. Chetcuti and co-workers have obtained the ^{13}C chemical shifts for a variety of heterobimetallic μ-alkyne complexes having the tetrahedrane geometry, **C**. These complexes show the two alkyne carbons falling within the range of δ 60 to 100 p.p.m.,[16] reminiscent of the deshielding effect of electron withdrawing groups on sp^3 hybridized carbon atoms.[17] In

contrast, the ^{13}C chemical shifts for the alkyne carbon atoms oriented colinear with the metal atoms tend toward lower field in the range of δ 120 to 150 p.p.m..[2a,18] Chemical shifts within this latter range are similar to those ^{13}C shifts observed for sp^2 hydridized carbon atoms of substituted alkenes[19] in keeping with the μ-η^1:$\eta^{1'}$-alkyne representation given to dimetallacyclobutene complexes, **D**. The ^{13}C n.m.r. spectrum of **13** exhibits a signal at δ 153.5 p.p.m. which can be assigned to the bridging alkyne carbon atom. The chemical shift is in the range expected for the μ-η^1;$\eta^{1'}$-bonding mode of the alkyne unit. This is the more attractive formulation for the structure of **13** since the resulting dimetallacyclobutene core, with a Ru-Ru bond, is now a well established structural form whereas alternative formulation **C**, containing the perpendicular alkyne unit without a supportive metal-metal bond, to our knowledge is unprecedented. In the carbonyl region compound **13** shows a single resonance at δ 203.9 p.p.m.. The apparent equivalence of all carbonyl ligands can be readily explained by the well known "merry-go-round" exchange process[12] which allows for facile scrambling of carbonyl groups lying in a plane, as is the case for these groups in the proposed structure **D**.

Although structure **D** is attractive, an unexpected feature of the alkyne carbon resonance at δ 153.5 p.p.m. is its triplet appearance. This would either imply that coupling between the alkyne carbon and both phosphorus nuclei is equal or that perhaps structural alternative **C**, which would be expected to give a triplet due to coupling to two equivalent phosphorus nuclei, is in fact correct. However, as discussed above the chemical shift data mitigate the latter possibility. An intriguing possibility is that the fluxional behaviour of **13** does not just involve CO scrambling but alkyne rotation as well via intermediates with structural form **C**, a process that would result in a triplet for the alkyne carbon resonance. Clearly it is highly desirable to obtain an X-ray structural resolution to this spectroscopic dilemma.

4.2.4. Further Reaction of 9 with Ethyne: Attempted Preparation of the Flyover Bridge Complex $Ru_2(CO)_4[\mu\text{-}(CHCH)_2C(O)](\mu\text{-dppm})$

The gentle refluxing of a THF solution of $Ru_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$, **9**, while purging with ethyne was monitored by IR spectroscopy for two hours and showed that no reaction had taken place. The starting material was recovered by removing the solvent *in vacuo*, and the IR spectrum of the resulting residue confirmed that no decomposition of the starting material, and no formation of any new product had taken place.

Irradiation of a hydrocarbon solution of **9** while purging with ethyne resulted in the rapid formation (ca. 10 minutes) of new products as shown by the IR spectrum in the carbonyl stretching region. The very poor solubility of **9** in either n-pentane or n-hexane prompted us to try other solvents. Irradiation of **9** in either benzene, toluene, or methylcyclohexane resulted in significantly longer reaction times (ca. 30 to 90 minutes) with methylcyclohexane requiring the smallest increase in irradiation time. An unfortunate result of the increase in irradiation time was an increase in the formation of a brown-black, insoluble substance (polyacteylene) which effectively coated the walls of the reaction vessel. To minimize the formation of polyacetylene the reactions were carried out under one atmosphere of ethyne with no apparent reduction in the conversion of **9** to products.

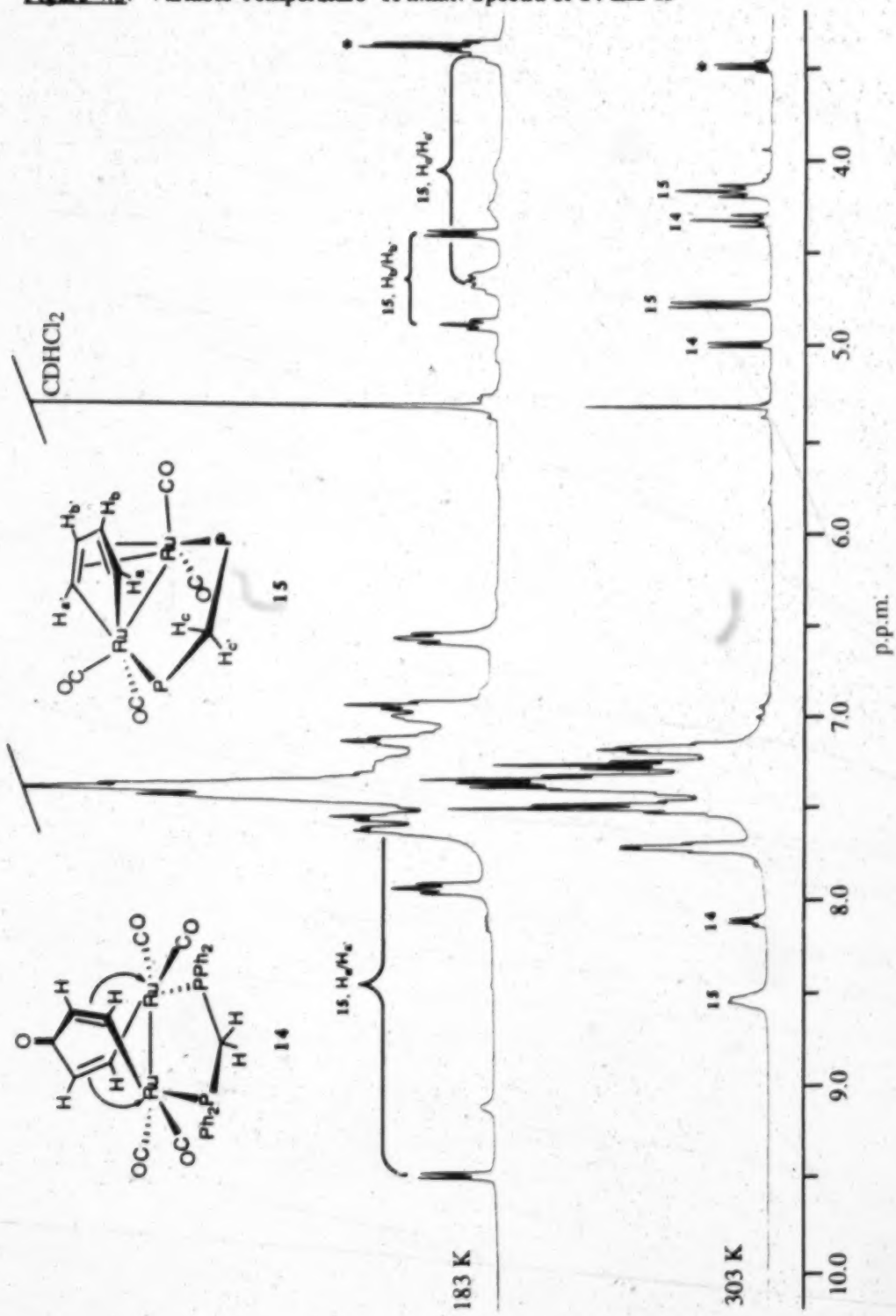
Removal of the solvent *in vacuo* from the reaction mixture yielded an off-white solid. The IR spectrum in the carbonyl stretching region of the solid showed peaks at 2036m, 2009vs, 1981s, 1967s, 1665m cm^{-1}. Of note is the shift of the ketonic carbonyl stretching frequency at 1712 cm^{-1} for the metallacyclopentenone,

9, to 1665 cm^{-1}. This shift to lower wavenumbers parallels the behaviour observed when $Fe_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$ ($\nu_{CO(ketonic)}$ = 1725 cm^{-1}) is irradiated in the presence of ethyne to give the flyover bridge species $Fe_2(CO)_4[\mu\text{-}(CHCH)_2C(O)](\mu\text{-dppm})$ ($\nu_{CO(ketonic)}$ = 1657 cm^{-1}).[2b]

The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra obtained at room temperature clearly showed the presence of two distinct, yet chemically similar species. In the ^1H n.m.r. spectrum there were three sharp signals at δ 8.14 (dt), 4.97 (d), and 4.28 (t) p.p.m. in a 1:1:1 integral ratio that can be assigned to one species (**14**), and three broad, poorly resolved signals at δ 8.57 (br), 4.75 (d, br), and 4.13 (br) p.p.m. in a 1:1:1 integral ratio that can be assigned to a second species (**15**). The relative amounts of **14**:**15** varied from one preparation to another thus providing a simple but effective check on the assignments made to each species. A typical ratio of **14**:**15** would be approximately 1:2.3. The $^{31}P\{^1H\}$ n.m.r. spectra mirrored the relative ratios of **14**:**15** found in the ^1H n.m.r. spectra, with broad singlets at δ 27.3 and 32.8 p.p.m. assigned to **14** and **15** respectively.

Warming the sample to 303 K enhanced the resolution of the two high field ^1H n.m.r. resonances attributed to **15** (δ 4.75 [d] and 4.13 [t,br]), but failed to resolve the broad peak at δ 8.57 p.p.m. (Figure 4.3). It should be noted that the doublet at δ 4.75 p.p.m. has an additional, small unresolved coupling. Care was taken not to overheat the sample as a precaution against decomposition. Selective ^{31}P-decoupled ^1H n.m.r. experiments were performed at 303 K which provided further confirmation of the initial assignments made to **14** and **15**. Irradiation of the ^{31}P resonance at δ 27.3 p.p.m. (**14**) caused the doublets of triplets at δ 8.14 p.p.m. to collapse to a doublet and the triplet at δ 4.28 p.p.m. to collapse to a singlet. The doublet at δ 4.97 p.p.m., also assigned to **14**, was not affected. Irradiation of the ^{31}P resonance at δ 32.8 p.p.m. (**15**) had little discernable affect

Figure 4.3: Variable Temperature ^{1}H n.m.r. Spectra of **14** and **15**



on the broad signal at δ 8.57 p.p.m., however it did collapse the broad triplet at δ 4.13 p.p.m. to a broad singlet.

The isolation of the flyover bridge diiron complex, $Fe_2(CO)_4[\mu\text{-}(CHCH)_2C(O)](\mu\text{-dppm})$,[2b] prepared via the u.v. irradiation of $Fe_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$ in the presence of an ethyne purge (28% yield), gave strong evidence in support of previous suggestions[7] that successive coordination of alkynes to metal carbonyls followed by carbon-carbon bond formation leads to the formation of cyclic organic molecules. The ^1H n.m.r. data observed for **14** is very similar to that found for the diiron flyover bridge complex (Table 4.3). The low field chemical shift observed for one of the ^1H resonances is typical[2a] for a hydrogen attached to a carbon that is σ-bonded to one metal and π-bonded to another, corresponding to the α-carbon of the pentadienone fragment illustrated in

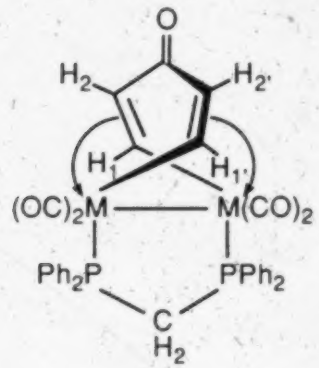
Table 4.3: Selected ^1H n.m.r. Data for Diiron and Diruthenium Flyover Bridge Complexes

Complex	^1H n.m.r δ (p.p.m.)[a,b]
$Ru_2(CO)_4[\mu\text{-}C_4H_4C(O)](\mu\text{-dppm})$ **14**	8.14 dt ($J_{HH} = J_{PH} = 7$, $(CHCH)_2CO$, 2H) 4.97 d ($J_{HH} = 7.2$, $(CHCH)_2CO$, 2H) 4.28 t ($J_{PH} = 10.5$, CH_2, 2H)
$Fe_2(CO)_4[\mu\text{-}C_4H_4C(O)](\mu\text{-dppm})$ [c]	8.17 dt ($J_{HH} = J_{PH} = 7$, $(CHCH)_2CO$, 2H) 3.86 d ($J_{HH} = 7$, $(CHCH)_2CO$, 2H) 4.57 t ($J_{PH} = 9$, CH_2, 2H)
$Ru_2(CO)_6[\mu\text{-}C_4H_4C(O)]$ [d]	8.62 d ($J_{HH} = 7$, $(CHCH)_2CO$, 2H) 4.95 d ($J_{HH} = 7$, $(CHCH)_2CO$, 2H)

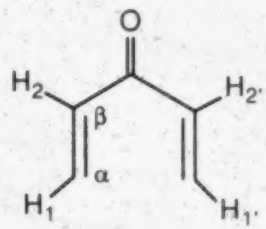
[a] Coupling constants in Hertz.
[b] Solvent: Dichloromethane-d_2
[c] a)Hogarth, G.; Kayser, F.; Knox, S. A.R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc. Chem. Comm.*, **1988**, 358 b) Hogarth, G., *PhD Thesis*, University of Bristol, **1986**, p. 268.
[d] Kiel, G.-Y.; Takats, J. *Unpublished Results*.

Figure 4.4 (b). The CH_1 and $CH_{1'}$ carbon atoms have μ-carbene character, causing the attached proton to resonate at low field. The chemical shifts observed for the CH_1 and $CH_{1'}$ protons are similar to those observed for a proton attached to a carbon σ-bound to a metal in dimetallacyclopentenone complexes,[2a] such as **9**, or the proton present on the μ-$CH(CH_3)$ group of *cis*-$(Cp)_2Ru_2(CO)_2(\mu\text{-}CMe_2)(\mu\text{-}CHMe)$, which resonates as δ 8.12 p.p.m..[20]

Figure 4.4: General $M_2(CO)_4[\mu\text{-}C_4H_4C(O)](\mu\text{-dppm})$ Flyover Complex and Corresponding Pentadienone Fragment



(a)



(b)

Based on a solid state structure,[21] the flyover bridge complex could be present in one of two enantiomeric forms, both having C_2 symmetry. From this structure (Figure 4.4 (a)) the H_1 proton would be expected to couple to one phosphorus of dppm and the $H_{1'}$ proton to the other phosphorus. From the selective ^{31}P-decoupled ^1H n.m.r. experiments it can be seen that H_1 and $H_{1'}$ are coupled equally to both phosphorus nuclei, an observation that may be attributed to fluxionality of the pentadienone fragment at room temperature. Indeed, this type of dynamic behaviour has been the subject of a recent study by Aime and co-workers for a series of flyover bridge complexes of the type $M_2(CO)_5(L)[\mu\text{-}(CPhCMe)_2C(O)]$ (M = Fe, Ru; L = CO, PPh_3, $AsPH_3$, or $SbPh_3$).[22] Earlier,

Hoffmann and Thorn[23] investigated the theoretical aspects of the possible bonding modes available to these types of complexes based on a fulvalene [μ-$(CH{=}CH)_2CH_2$] type fragment bridging two metals together, with the conclusion that the flyover structure gave the most favourable interaction with an $Fe_2(CO)_6$ fragment. Taking these two works in concert led to the conclusion that the pentadienone fragment may move through a transition state of C_{2v} symmetry.[22] In the case of **14**, or the diiron analogue, this transition state would result in an averaging of the H_1 and $H_{1'}$ environments between the two phosphorus nuclei. The additional coupling between H_1 and H_2, and $H_{1'}$ and $H_{2'}$, would then give the observed doublets of triplets splitting to the resonance. As the temperature is lowered in the ^1H n.m.r. experiment, all three signals broaden and merge with the baseline, but fail to re-emerge even at 183 K. By using the results of the X-ray diffraction studies of several $Fe_2(CO)_6[\mu\text{-}(CRCR)_2R']$ (R = Ph, R' = CO;[21a] R = Me, R' = CO;[21b] R = H, R' = CH_2[21c]) as a guide, the structure of **14** and its fluxional behaviour are proposed below in Scheme 4.1.

Before proposing a plausible structure for **15** we would like to recall that besides the flyover bridging type of complexes two other structural forms are also commonly observed to arise from the reaction of metal carbonyls with alkynes. There are many examples of metallacyclopentadienes[24,25] and a few metallacyclohexadienones[26,2a] reported in the literature. With these two structural types one metal atom forms two σ-bonds with the terminal carbon atoms of the diene, while the other metal atom forms two π-bonds with the diene carbons (Figure 4.5). An interesting feature of the crystal structure of the metallacyclohexadienone, $Cp_2Fe_2(CO)[\mu\text{-}C_4R_4C(O)]$ (R = CF_3),[24] is that the ketonic carbonyl is bent out of the diene plane, away from the iron centre. The strong electron withdrawing substituents (CF_3) on the pentadienone fragment causes a decrease in the electron

Scheme 4.1: Dynamic Behaviour of Diruthenium Flyover Complex, **14**

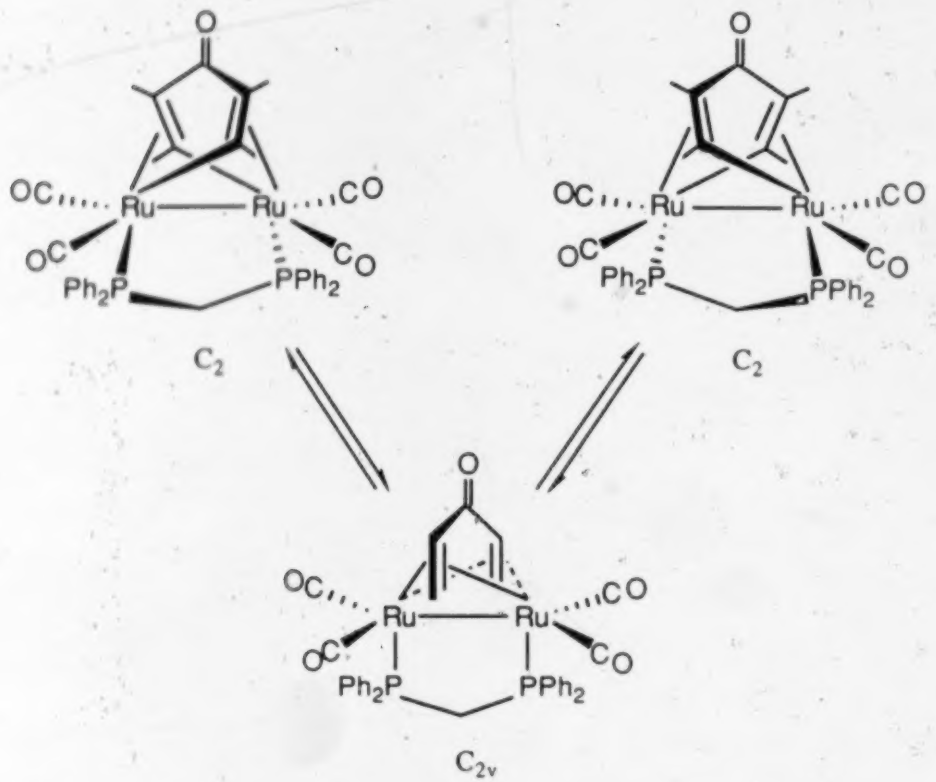
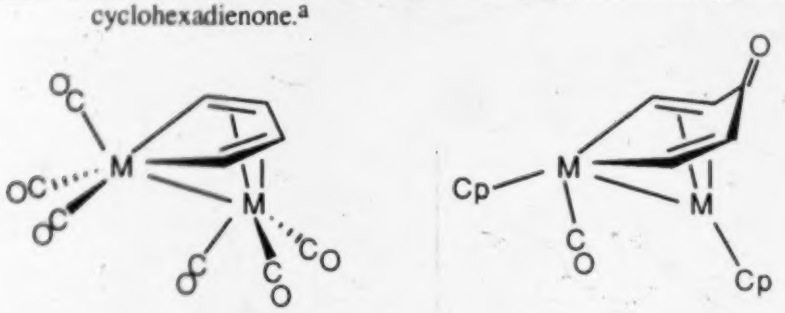


Figure 4.5: General Representations for: (a) Metallacyclopentadiene; (b) Metallacyclohexadienone.[a]



(a) (b)

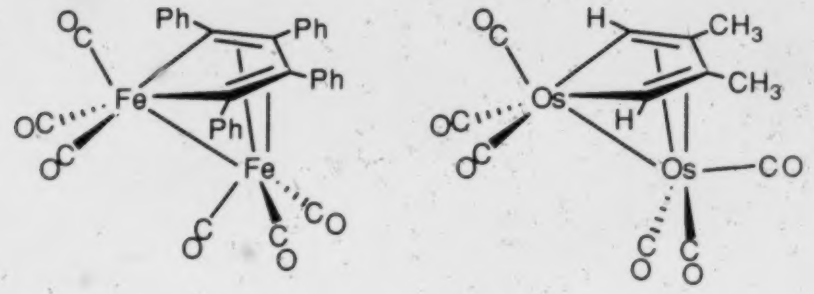
[a] *Substituents on diene carbon atoms omitted for clarity (M = Fe).*

density on the diene carbon atoms. This decrease of electron density results in a stronger metal-carbon interaction between iron and the diene carbons which will render these carbon atoms sp^3 in character. This sp^3 character is readily observed in the out of plane bending of the ketonic carbonyl above the diene plane. By bending the ketonic carbonyl out of the diene plane, away from the metal, an otherwise unfavourable interaction between the ketonic carbon and the metal may be reduced. Indeed, this result parallels the unfavourable interaction calculated for a fulvalene,[23] or a planar cyclopentadienone fragment,[22] with the $Fe_2(CO)_6$ fragment. Other metallacyclohexadienone complexes, $Cp_2Fe_2(CO)[\mu\text{-}(C_2R_2)_2C(O)]$ (R = H; Me; CO_2Me; CF_3), reported by Knox and co-workers,[2a] also tend to have electron withdrawing substituents on the pentadienone fragment suggesting that these substituents afford a similar interaction to that proposed for the diiron complex to give a stable product.

When alkynes that do not have electron withdrawing substituents are allowed to react with metal carbonyls the products appear to favour either the metallacyclopentadiene or the flyover bridge stucture. Thus the reaction of diphenylacetylene with $Fe(\eta^4\text{-CHT})(CO)_3$ yields the metallacyclopentadiene bridged complex, $Fe_2(C_4Ph_4)(CO)_6$,[25e] while reaction with $Fe_2(CO)_9$ yields the flyover bridge complex, $Fe_2[C_4Ph_4C(O)](CO)_6$.[21a] Both of these complexes have been structurally characterized by X-ray diffraction.

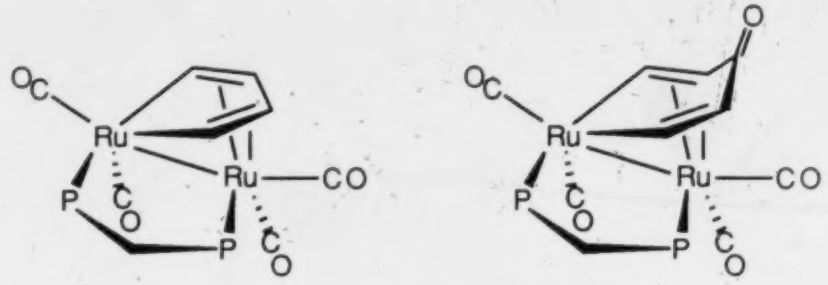
A metal dependence for the geometry of the carbonyl ligands about each metal centre for the $M_2(CO)_6$ (M = Fe,[25e] Os[26a]) fragment has been observed in the X-ray diffraction studies of two metallcyclopentadiene derivatives. In the iron case the molecule adopts the structure depicted in Figure 4.6 (a), while in the osmium case the carbonyls are in a saw-horse geometry, (Figure 4.6 (b)).

Figure 4.6: Example of the Different Geometries Observed for Metallacyclopentadiene Derivatives



(a) (b)

Accordingly we can propose two structures for compound **15** based on the structures in Figure 4.5 simply by replacing two of the carbonyl ligands with a bridging dppm ligand.



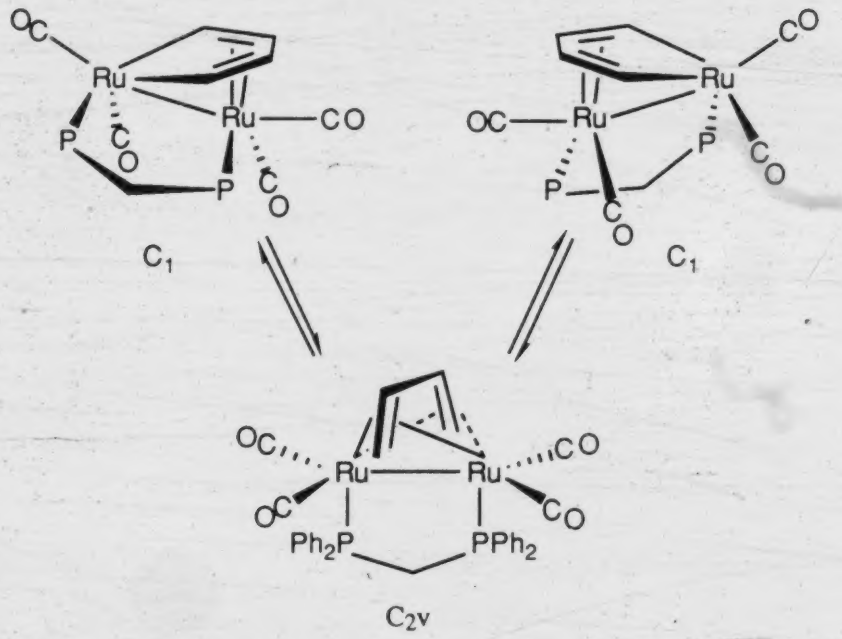
(E) **(F)**

On the basis of previous observations which showed that the hexadienone structure is preferred mostly with electron withdrawing substituents on the alkynes, we propose that the metallacyclopentadiene structure, **E**, will be favoured for **15**. In this arrangement all the hydrogens of the pentadiene fragment would be distinct. The fact that only two signals are observed in the room temperature ^{1}H n.m.r. spectrum for the pentadiene fragment of **15** suggests that the molecule is fluxional.

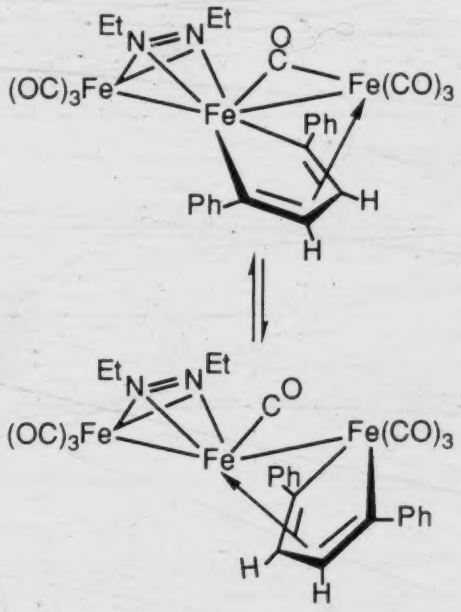
Indeed as the sample is cooled all three peaks assigned to **15** in the ^1H n.m.r. spectrum broaden and merge with the baseline at the same rate. Below 233 K the peaks begin to re-emerge. Careful observation of the peaks due to **14** show that they are still slowly broadening and merging with the baseline below 233 K, thus leaving the spectrum of **15** relatively uncomplicated. In the high field region of the ^1H n.m.r. spectrum obtained at 183 K there are two broad multiplets at δ 4.65 and 3.40 p.p.m., a doublets of doublets at δ 4.90, and a doublet at δ 4.39 p.p.m.. Allowing for a slight dependence of the chemical shifts on temperature, the weighted average of the pair of multiplets, and that of the doublets of doublets correspond to the methylenic triplet at δ 4.13 p.p.m. and the doublet at δ 4.75 p.p.m., respectively, in the room temperature ^1H n.m.r. spectrum. Under the same consideration one would expect the broad low field peak at δ 8.57 p.p.m. in the room temperature ^1H n.m.r. spectrum to be the weighted average of two peaks in the near-limiting spectrum at 183 K. A doublet is observed in the 183 K ^1H n.m.r. spectrum at δ 9.48 p.p.m.. Assuming that this resonance would coalesce with another to give rise to the broad peak observed in the room temperature ^1H n.m.r. spectrum, one may predict the second peak to resonate at approximately δ 7.4 p.p.m., a position that would be masked by the phenyl region and prevent this peak from being observed. These observations may be explained in Scheme 4.2 where we postulate that **15** passes through an intermediate containing a mirror plane such that the environments for each of the three groups of hydrogens are averaged.

Site exchange of the C_4 ring of metallacyclopentadienes, passing through an intermediate of C_{2v} symmetry, has been suggested in the past.[27] This dynamic behaviour is the subject of a recent article in which the two metal centres involved in the site exchange are in different environments[28] (Scheme 4.3). The chemically

Scheme 4.2: Dynamic Behaviour of Diruthenium Complex, **15**



Scheme 4.3: Dynamic Behaviour of a Ferracyclopentadiene



non-equivalent metal centres enabled the authors to readily observe the inter-conversion of the two distinct isomers at high temperatures using ^1H n.m.r. spectroscopy. The 1,4-diphenyl-butadiene fragment used in the investigation was found to isomerize between the two metal centres such that the carbon atoms with the phenyl substituents were always σ-bound to one metal or the other (Scheme 4.3). This observation suggests that a transition state similar to that proposed by Hoffmann for the interaction of a butadiene fragment with an $Fe_2(CO)_6$ fragment (with C_{2v} symmetry) may exist.[23]

The proposed alternative structure for **15**, the metallacyclohexadienone complex, **F**, would also have to be fluxional in order to account for the ^1H n.m.r. features. However, a simple fluxional process for this structure would require that the metallacyclohexadienone pass through the same intermediate as the flyover complex which seems unreasonable, lending further support to the metallacyclopentadiene formulation.

4.3. Experimental Section

4.3.1. Starting Materials and Reagents

$Ru_2(CO)_7(\mu$-dppm), **2**, was prepared by method a) as outlined in Chapter Two. Ethyne (acetylene) was obtained from Union Carbide Inc. (Canada). Dimethylacetylene dicarboxylate (dmad) and diphenylacetylene were purchased from Aldrich Chemical Company and used as received. ^{13}C-enriched carbon monoxide (99.1%) was purchased from Isotec (Matheson) Inc.

4.3.2. Synthetic Procedures

$Ru_2(CO)_5[\mu\text{-}CHCHC(O)](\mu\text{-}dppm)$, 9

$Ru_2(CO)_7(\mu\text{-}dppm)$, **2**, (51 mg, 0.0652 mmole) was dissolved in dichloromethane (15 ml) under an argon atmosphere and the solution cooled to 0°C in an ice bath. Ethyne was slowly passed through the solution via a #22 gauge needle and the solution stirred at room temperature in the dark. The acetone stabilizer present in the ethyne was removed by first passing the ethyne through a Dry Ice/acetone-cooled cold trap. The reaction was monitored by IR spectroscopy until all **2** was consumed (ca. 15 minutes), and complete conversion to product observed with ν_{CO} bands at 2057s, 1996(sh), 1989vs, 1968s, 1939m, 1714w cm^{-1}. The solvent was removed *in vacuo* at 0°C to yield a red-brown residue. The residue was dissolved in dichloromethane (ca. 1-2 ml) and pentane added until a precipitate formed. The mixture was then cooled to -78°C for one hour and the precipitated product recovered by filtering off the supernatant liquid and drying the precipitate *in vacuo* at room temperature. The resulting light yellow-brown powder of **9** was washed with three consecutive, two millilitre portions of pentane, and finally dried *in vacuo* at room temperature (32 mg, 62.9% yield).

$Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^{1'}\text{-}C_2(CO_2CH_3)_2](\mu\text{-}dppm)$, 12

$Ru_2(CO)_7(\mu\text{-}dppm)$ (18 mg, 0.024 mmole) was dissolved in THF (5 ml) under an argon atmosphere. A two-fold excess of dimethylacetylene dicarboxylate (dmad) (5 µl, 0.050 mmole) was added to the solution and the mixture stirred in the dark at room temperature for one hour. The IR spectrum of the solution showed

complete consumption of the starting material with new ν_{CO} bands at 2070s, 2034s, 2006s, 1986s, 1968(sh), 1709vw, 1692w cm^{-1}. The solvent was removed *in vacuo* at room temperature and the resulting red-orange residue redissolved in THF (1 ml). (Attempts to remove unreacted dmad by passing the crude product over a silica gel column were thwarted by low yields of product resulting from decomposition of the product on the column.) The product was precipitated from THF by addition of pentane (5 ml), followed by cooling of the flask and its contents to -78°C. The supernatant liquid was decanted and the precipitated product dried *in vacuo* at room temperature to give **12**, an orange-yellow crystalline solid, in 53% yield.

Analysis Calculated for $Ru_2C_{37}H_{28}O_{10}P_2$: C, 49.56%; H, 3.15%; Found: C, 49.20%; H, 3.61%.

IR (THF, ν_{CO}): 2070s, 2034s, 2006s, 1986s, 1968(sh), 1709vw, 1692w cm^{-1}.

^1H n.m.r. (CD_2Cl_2, 298 K): δ 7.1-7.7 (m, 20H, C_6H_5), 4.56 (dt, 1H, CH_2, J_{PH} = 11.6, J_{HH} = 13.4 Hz), 3.33 (dt, 1H, CH_2, J_{PH} = 11.6, J_{HH} = 13.4 Hz), 3.31 (s, 6H, CH_3).

$^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 20.3 (s).

$^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 203.1 (d, 2CO, J_{PC} ≈ 5 Hz), 198.6 (AA'XX', 2CO, J_{PC} = 99.5, $J_{P'C}$ = 2.5, $J_{PP'}$ = 56.0 Hz), 191.8 (d, 2 CO, J_{PC} = 5.3 Hz), 171.6 (s, $C(O)OCH_3$), 128.5 - 134.1 (Phenyl Region), 51.2 (s, CH_3).

$Ru_2(CO)_6[\mu\text{-}\eta^1\text{:}\eta^{1'}\text{-}C_2(Ph)_2](\mu\text{-dppm})$, 13

$Ru_2(CO)_7(\mu\text{-dppm})$, **2**, (55 mg, 0.070 mmole) was dissolved in THF (8 ml) under an argon atmosphere. This solution was transferred under argon to a three-neck round bottom flask (25 ml) fitted with a gas inlet and a water-cooled

reflux condenser. In another flask diphenylacetylene (14.3 mg, 0.0803 mmole) was dissolved in THF (1 ml) under an argon atmosphere. The diphenylacetylene solution was then inverse filtered to the solution of **2**, and the mixture kept in the dark. The mixture was warmed in an oil bath to 50-52°C and stirred at this temperature for 10.5 hours. The reaction was monitored by IR spectroscopy, specifically for the disappearance of the ν_{CO} bands of **2** at 2054 cm^{-1}. The solvent was removed *in vacuo* at room temperature to yield a red-yellow oily residue. The oil was dissolved in a minimum of THF and chromatographed on a florisil column, (3 x 13 cm) eluted with THF hexane (1:1) until the first band is half way down the column. The eluant was then changed to THF and the first band collected. Some decomposition on the top of the column was evident. The solvent was removed *in vacuo* at room temperature from the solution collected from the column and an oily residue obtained. The residue was washed once with pentane (ca. 2 ml) and the resulting solid dried *in vacuo* at room temperature to yield **13** as a fine, yellow powder. Yield: 45-56%.

Analysis Calculated for $Ru_2C_{45}H_{32}O_6P_2$: C, 57.94%; H, 3.45%; Found: C, 57.86%; H, 3.42%.

IR (CH_2Cl_2, ν_{CO}): 2025s, 1991vs, 1968m cm^{-1}.

^1H n.m.r. (CD_2Cl_2, 298 K): δ 6.8-7.5 (m, 30H, C_6H_5), 3.53 (t, 2H, CH_2, J_{PH} = 9.5 Hz).

$^{31}P\{^1H\}$ n.m.r. (CD_2CL_2, 298 K): δ 37.4 (s).

$^{13}C\{^1H\}$ n.m.r. (CD_2CL_2, 298 K): δ 203.9 (s, CO), 153.5 (t, *C*Ph, J_{PC} = 6.4 Hz), 136.6 (t, *ipso* C dppm, J_{PC} = 20.8 Hz), 131.8 (t, *ortho* C dppm, J_{PC} = 6.8 Hz), 131.0 (s, *para* C dppm), 129.1 (t, *meta* C dppm, J_{PC} = 4.9 Hz), 128.8 (d, *ipso* C Ph_2C_2, J_{PC} = 6.0 Hz), 127.9 and 127.7 (s, *ortho*/*meta* C Ph_2C_2), 123.7 (s, *para* C Ph_2C_2), 45.6 (t, *C*H_2, J_{PC} = 23 Hz).

Attempt to Prepare $Ru_2(CO)_4[\mu\text{-}(CHCH)_2C(O)](\mu\text{-dppm})$, 14

$Ru_2(CO)_5[\mu\text{-}C_2H_2C(O)](\mu\text{-dppm})$, **9**, (45 mg, 0.058 mmole) was dissolved in methylcyclohexane (140 ml) under an argon atmosphere. The solution was degassed by two freeze-pump-thaw cycles, and then transferred under argon to an immersion well cooled to -25°C. Ethyne was first passed through a Dry Ice/acetone cold trap to remove traces of acetone stabilizer and was then slowly bubbled through the solution in the immersion well. While purging with ethyne, the solution was irradiated ($\lambda_{max} \geq 370$ nm) at -25°C for approximately 45 minutes. The progress of the reaction was monitored by IR spectroscopy until all of **9** was consumed (ν_{CO}: 2056s, 2024vw, 2009s, 1996vs, 1971s, 1950m, 1740m cm^{-1}) and the new products formed, (ν_{CO}: 2035s, 2011vs, 1986s, 1970s, 1684w cm^{-1}). When the reaction was complete the solution was filtered and then transferred to a round bottom flask and the solvent removed *in vacuo*, at 0°C, in the dark. The product was extracted from the resulting yellow-brown residue into diethyl ether (10 ml). The ether solution was filtered (IR, ν_{CO}: 2033s, 2009vs, 1983s, 1968s, 1682w cm^{-1}) and the solvent removed *in vacuo* at 0°C to yield a yellow-white solid. The solid was washed with pentane and dried *in vacuo* to yield an inseparable mixture of $Ru_2(CO)_4[\mu\text{-}(CHCH)_2C(O)](\mu\text{-dppm})$, **14**, (ca. 12%), and $Ru_2(CO)_4[\mu\text{-}(CHCH)_2](\mu\text{-dppm})$, **15**, (ca. 28%). Reported yields are estimated from the relative integral ratios in the ^1H n.m.r. spectrum (298 K) and are based on ruthenium.

IR (CH_2Cl_2, ν_{CO}): **14** and **15**: 2036s, 2022s, 2009vs, 1981s, 1967s, 1665w.

^1H n.m.r. (CD_2CL_2, 303 K): **14**: δ 8.14 (dt, 2H, $[CHCH]_2CO$, $J_{HH} = 9$, $J_{PH} = 7$ Hz), 7.2-7.85 (m, phenyls), 4.97 (d, 2H, $[CHCH]_2CO$, $J_{HH} = 7.2$ Hz), 4.28 (t, 2H, CH_2, $J_{PH} = 10.5$ Hz); (CD_2Cl_2, 308 K): **15**: δ 8.57 (dt, 2H, $Ru[CHCH]_2$,

J_{HH} = 9, J_{PH} = 7 Hz), 7.2-7.85 (m, phenyls), 4.75 (dt, 2H, Ru[CHC*H*]$_2$, J_{HH} = 9, J_{PH} = 1.5 Hz), 4.13 (t[br], 2H, CH_2, J_{PH} = 11 Hz).

$^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 303 K): **14**: δ 27.3 (s[br]); **15**: δ 32.8 (s[br]).

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Chapter Five

Reaction at the Methylene Bridge of $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-}dppm)$

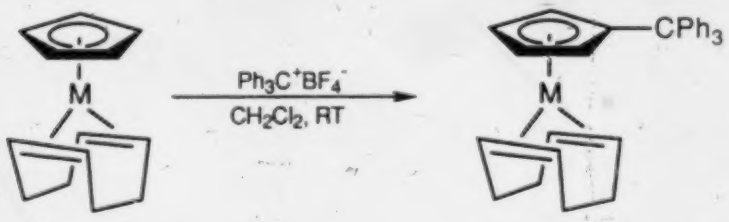
5.1. Introduction

The synthesis and derivative chemistry of transition metal complexes containing the μ-CH, μ-CH_2, and μ-CH_3 groups continues to attract a great deal of attention,[1] especially in view of the well established relevance of such species to the Fischer-Tropsch synthesis of hydrocarbons.[2] Casey and co-workers[1a] have successfully prepared the diiron complex $[CpFe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)]^+$ via protonation of $CpFe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ with either CF_3SO_3H or $HBF_4{\cdot}Et_2O$. More recently Knox and co-workers[3] isolated the analogous complexes $[Cp_2Ru_2(CO)_3(\mu\text{-}CH_3)]^+$ and $[Cp_2Ru_2(CO)(\mu\text{-}CH_3)(\mu\text{-}dppm)]^+$ which they obtained by protonation of the corresponding methylene-bridged precursors with CF_3CO_2H and $HBF_4{\cdot}OEt_2$ respectively.

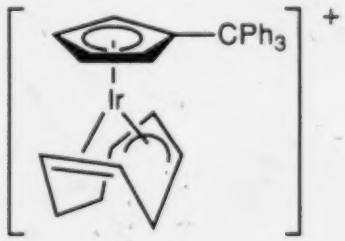
The use of triphenylmethyl cation, or trityl, as a hydride abstractor from transition metal complexes has been known for several decades.[4] Casey successfully showed that treatment of the complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ with trityl hexafluorophosphate gave $[Cp_2Fe_2(CO)_3(\mu\text{-}CH)]^+$.[1a] However, Knox[3] was unable to prepare $[Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}CH)(\mu\text{-}dppm)]^+$ by treating $Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}dppm)$ with trityl. Instead it was discovered that $[Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}CH_3)(\mu\text{-}dppm)]^+$ readily loses H_2 in THF to give the μ-CH^+ derivative. Trityl-mediated hydride abstractions to produce a μ-CH^+ moiety have not been without their difficulties. Casey notes that the treatment of *cis*-$Cp_2Fe_2(NO)_2(\mu\text{-}CH_2)$ with trityl gave a mixture of products, affording the crude, cationic bridging methyne complex in only 25% yield.[5]

Other than hydride abstraction, reaction of trityl with transition metal complexes are also well documented. The reaction of one equivalent of trityl with CpM(COD) (M = Rh, Ir), Scheme 5.1, leads to its incorporation into the cyclopentadienyl ligand.[6] It is only when CpM(COD) is treated with two

Scheme 5.1: Reaction of Cyclopentadiene Ligand with Triphenylmethyl Cation

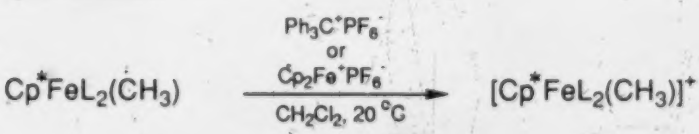


equivalents of trityl that hydride abstraction from the COD ligand occurs, however, the incorporation of trityl into the cyclopentadienyl ligand is still observed in the final product,[6]



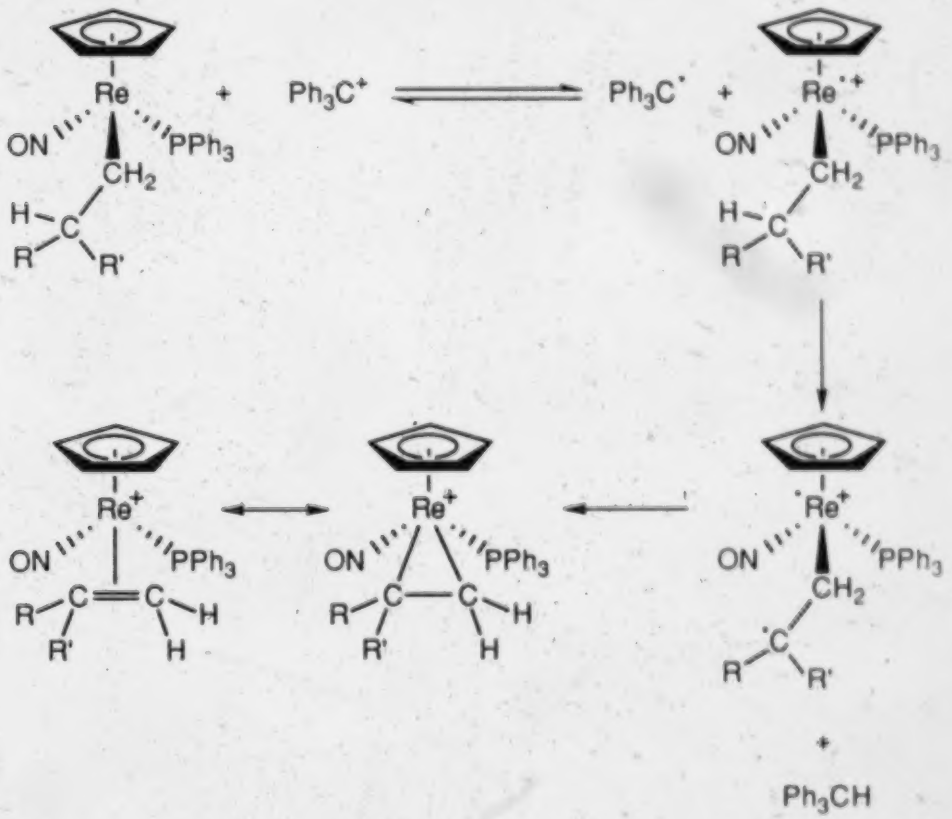
Another, common reaction of trityl is its behaviour as a one-electron oxidant similar to ferricinium ion (Cp_2Fe^+). A recent example of this type of reaction is shown below in Scheme 5.2.[7]

Scheme 5.2: Oxidation of Fe^{II} to Fe^{III} Using Ph_3C^+ (L = $P(OMe)_3$, $^1/_2$ dppe)



Evidence for radical-based reactions involving trityl have been reported in recent years. The mechanism of the reaction of Ph_3C^+ with transition metal complexes has been examined by Gladysz and co-workers.[8] It was shown that the reaction proceeds via one electron oxidation to give an intermediate metal cation radical ($M^{\bullet+}$) and a triphenylmethyl radical ($Ph_3C^{\bullet}$). The latter goes on to abstract a hydrogen atom and forms Ph_3CH, while the radical complex intermediate rearranges to give the η^2-alkene complex (Scheme 5.3).

Scheme 5.3: Proposed Mechanism for Radical-Initiated β-Hydride Abstraction



The successful protonation of a μ-methylene ligand to the μ-methyl group on a diruthenium complex by Knox,[3] and on a diiron complex by Casey,[1a] together

with the relatively robust nature of **10**, encouraged us to attempt to protonate this complex as well. The abstraction of a hydride from the μ-methylene ligand of **10** using trityl tetrafluoroborate was also attempted in the hope of obtaining the cationic μ-methyne complex.

5.2. Synthesis and Characterization

5.2.1. Protonation Reactions

A dichloromethane solution of $Ru_2(CO)_6(\mu\text{-}CH_2)$(dppm), **10**, was treated with an excess of CF_3CO_2H and allowed to stir in the dark at room temperature for several hours. The initial red-orange colour of the solution slowly lightened to yellow-orange. The course of the reaction was monitored by IR spectroscopy which showed consumption of **10** and formation of two new, very broad bands in the terminal carbonyl stretching region. Once the reaction was thought to be complete the solvent was removed *in vacuo* at 0°C yielding a yellow-brown solid. The solid was washed with n-pentane or n-hexane and the residue extracted into a minimum volume of diethyl ether. The IR spectrum showed bands at 2076s,br, 2018s,br, and 1974m,br cm^{-1}. Attempts to precipitate the product yielded only small amounts of material.

Since the yield of product from the reaction of **10** with CF_3CO_2H was poor the protonation was attempted using $HBF_4{\cdot}OEt_2$. Stirring together $Ru_2(CO)_6(\mu\text{-}CH_2)$(dppm) with one equivalent of $HBF_4{\cdot}OEt_2$ in dichloromethane at room temperature resulted in a slow, but smooth conversion to a new product as indicated by the IR spectrum. A significant shift of the carbonyl stretching frequencies to higher energy in the IR spectrum indicated a higher CO bond order as expected for the formation of a cationic complex. The carbonyl stretching frequencies observed

for the new product appeared at 2127w, 2080s, 2052m, and 2022m,br cm^{-1}. The solvent was removed *in vacuo* at 0°C to yield a yellow residue. The residue was washed with small protions of n-pentane or n-hexane and then dried *in vacuo* at room temperature to yield a golden-yellow cystalline solid.

The ^1H n.m.r. spectrum of the product was obtained and showed some unusual features. First the phenyl region extended from δ 6.3 to 8.1 p.p.m., and is comprised of a series of multiplets. Two doublets of triplets are also observed, one at δ 4.32 p.p.m. and the other at δ 4.53 p.p.m., which are most probably due to the methylenic protons on dppm. The resolution of the spectrum was poor, however, and no other peaks could be assigned with confidence. The expected range for a μ-CH_3^+ moiety, based on the analogous diiron and diruthenium cyclopentadienyl complexes,[1a,2] is at high field in the range of δ -1 to -2 p.p.m.. No peaks were observed above δ 0 p.p.m.. Keeping in mind that the loss of H_2 in solution to give the μ-CH^+ species has been observed by Knox[3] the ^1H n.m.r. spectrum was also obtained down to δ 20 p.p.m., however, no peaks were observed in this region.

Treatment of a dichloromethane solution of **10** with an excess of $HBF_4{\cdot}OEt_2$ apparently resulted in the formation of additional product(s) as evidenced by the appearance of an additional ν_{CO} band at 2110 cm^{-1}.

Initially the protonation reaction appeared promising, however, the difficulties encountered when attempting to isolate a pure product led the author to abandon further work in this area.

5.2.2. Hydride Abstraction

Addition of one equivalent of $Ph_3C^+BF_4^-$ to a dichloromethane solution of $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$ resulted in the rapid formation of a new product as evidenced by IR spectroscopy. The carbonyl stretching frequencies shifted to

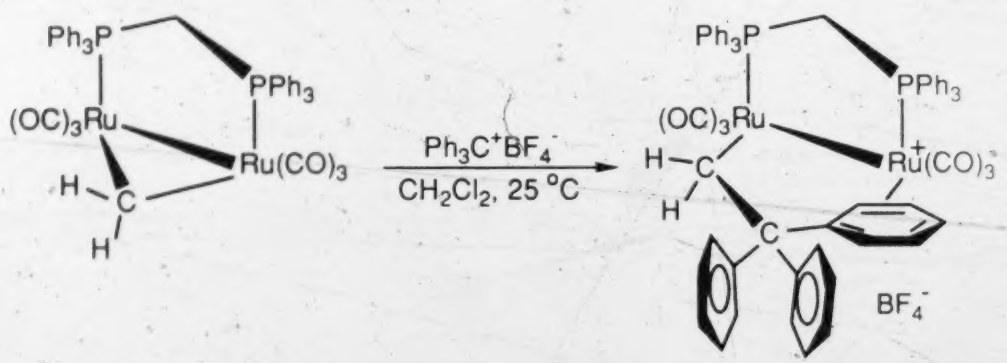
higher energy from 2055s, 2016s, 1985m, 1955m,br cm^{-1} to 2099s, 2065s, 2019s, and 2005(sh) cm^{-1}. Removal of the solvent *in vacuo* at room temperature gave a yellow residue. The residue was washed with small amounts of n-pentane or n-hexane and then dried *in vacuo* to give a yellow-tan solid. This solid was only sparingly soluble in diethyl ether and insoluble in hydrocarbon solvents. The solid was dissolved in dichloromethane, to which n-pentane or n-hexane was then added, and the mixture cooled slowly overnight in an attempt to induce cystallization. No crystallization was observed. However, upon obtaining the IR spectrum of the solution the stability of the initial product was immediately suspect because new bands at 2127w, 2080s, 2051s, and 2000m,br cm^{-1} appeared. In a subsequent experiment it was observed that prolonged stirring of the reaction solution at room temperature, in the dark, would slowly convert the initial product to the second product over a period of approximately twelve hours. When no further reaction was apparent the solvent was removed *in vacuo* at 0°C, the resulting residue washed with n-pentane or n-hexane, and then dried to yield a pale yellow solid. The IR spectrum of the product, obtained in CH_2Cl_2, had carbonyl stretching frequencies at 2127m, 2079s, 2051s, 2017m cm^{-1}.

The ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of this final product were also obtained. The $^{31}P\{^1H\}$ n.m.r. spectrum displayed two doublets, one at δ 14.7 p.p.m. and the other at δ 3.8 p.p.m., with a P-P coupling of 58.8 Hz each. Both the IR and ^1H n.m.r. spectra had some features in common with those observed for the product obtained from the reaction of **10** with $HBF_4{\cdot}OEt_2$. The phenyl region is quite broad, extending from δ 6.3 to 8.1 p.p.m.. The methylenic protons of dppm are assigned to the doublets of triplets at δ 4.31 p.p.m. (J_{HH} = 14.6, J_{PH} = $J_{P'H}$ = 8.3 Hz) and δ 4.54 p.p.m. (J_{HH} = 14.6, J_{PH} = 11.0, $J_{P'H}$ = 12.5 Hz), with each signal integrating to one hydrogen relative to approximately thrity-five hydrogens for the phenyl region. The P-H coupling constants were determined by

selective ^{31}P-decoupled ^{1}H n.m.r. experiments. A broad peak at δ 2.95 p.p.m. was also observed and integrated to two hydrogens relative to each of the signals assigned to the methylenic protons of dppm. Neither broad band nor selective ^{31}P-decoupling experiments had any observable affect on the broad signal at δ 2.95 p.p.m.. Cooling the sample to 187 K served only to further broaden the signals in the ^{1}H n.m.r. spectrum.

The $^{13}C\{^{1}H\}$ n.m.r. spectrum displayed a doublets of doublets at δ 35.6 p.p.m. (J_{PC} = 27 Hz) in the region expected for the methylene carbon of dppm. In addition to this signal there was a singlet at δ 82.2 p.p.m.. This peak is approximately 9 p.p.m. to low field of the chemical shift observed for the bridging methylene group in $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$, **10**.[9] Insertion of the electrophilic Ph_3C^+ cation into one of the metal-carbon bonds of the bridging methylene ligand could result in a substantial deshielding of the CH_2 carbon atom as observed in the ^{13}C n.m.r. spectrum. In order to satisfy the electron deficient ruthenium a two electron donation from one of the phenyl groups on the trityl to the metal atom is proposed (Scheme 5.4). This η^2-bonding interaction is unusual, and

Scheme 5.4: Reaction of Trityl with $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$



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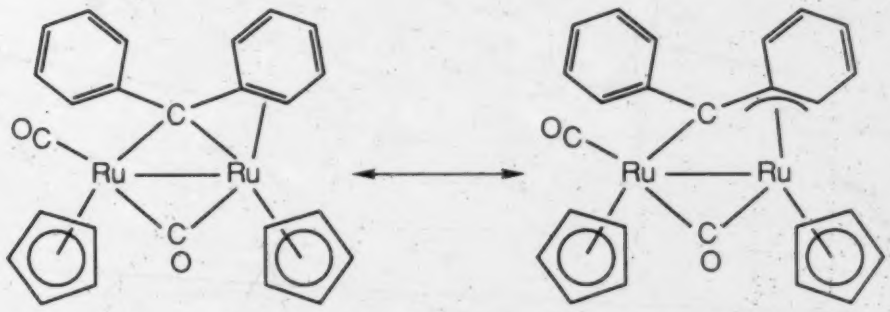
to our knowledge a similar interaction has not been reported in the literature, although a related η^2-arene interaction has been postulated by Sweet and Graham in $[CpRe(NO)(CO)(Ph_3CH)]^+$.[10] The lack of an available orbital on the methyl carbon of trityl excludes an η^3-benzyl[11] type interaction that have been observed on the diphenylmethylene-bridged dinuclear complexes $[Cp_2Ru_2(CO)_2(\mu\text{-}\eta^3\text{-}CPh_2)]$,[12] and $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^3\text{-}CPh_2)]$[13] (Figure 5.1). The complexity of the

Figure 5.1: Resonance Forms for η^3-Benzyl of $[Cp_2Ru_2(CO)_2(\mu\text{-}\eta^3\text{-}CPh_2)]$



phenyl region in both the ^1H and the $^{13}C\{^1H\}$ n.m.r. spectra provide further evidence that suggest the possibility of incorporation of trityl into the complex in this manner. In an attempt to demonstrate that the trityl does not readily attack the dppm ligand, and that the facile reactivity of **10** is due to the presence of the μ-CH_2 moiety, the following experiment was undertaken: a dichloromethane solution of $Ru_3(CO)_{10}(\mu\text{-dppm})$ was stirred together with one equivalent of trityl, in the dark, at room temperature for one day. An aliquot of the reaction mixture was sampled every few hours and the IR spectrum obtained. The IR spectra showed no evidence for the reaction of trityl with the dppm ligand to form a cationic complex.

5.3. Conclusions

Compound **10** reacts readily with protonating reagents and triphenylmethyl cation, however, formation of either a μ-CH_3^+, or a μ-CH^+ unit, respectively, does not appear to be favoured. Both reactions are complex and the true nature of the resulting product can only be speculated on. Further investigation of these reactions is warranted, especially the reaction with trityl which may provide further insight into the possible reaction pathways available to methylene-bridged transition metal complexes with trityl cation.

5.4. Experimental Section

5.4.1. Starting Materials and Reagents

$Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$, **10**, was prepared by reaction of a dichloromethane solution of $Ru_2(CO)_7(\mu\text{-dppm})$, **2**, with an etheral solution of diazomethane at -78°C.[9] Trityl fluoroborate ($Ph_3C^+BF_4^-$) was purchased from Aldrich Chemical Company and used as received.

5.4.2. Synthetic Procedures

Attempt to Hydride Abstract at the Methylene Bridge of $Ru_2(CO)_6(\mu\text{-}CH_2)(\mu\text{-dppm})$, 10

$Ru_2(CO)_6(\mu\text{-}CH)_2(\mu\text{-dppm})$, **10**, (46.7 mg, 0.0608 mmole) was dissolved in dichloromethane (8 ml) under an argon atmosphere and the solution cooled to -25°C. In a separate flask trityl fluoroborate (19.1 mg, 0.0578 mmole) was

dissolved in dichloromethane (2 ml), under an argon atmosphere, and was then transferred to the cold solution of **10**. The mixture was stirred in the dark while the progress of the reaction was monitored by IR spectroscopy. The reaction mixture was allowed to slowly warm to room temperature (ca. 1 $^1/_2$ hours) and was stirred at room temperature for eight and one half hours, after which time the IR spectrum of the solution showed complete consumption of **10** and the formation of a new product, **16**, with carbonyl stretching frequencies at 2127w, 2079s, 2051s, 2017m cm^{-1}. The solvent was removed *in vacuo* at 0°C. The resulting residue was washed with n-pentane and then dried *in vacuo* at room temperature to yield **16** as a yellow-white solid in 49% yield.

IR (CH_2Cl_2, ν_{CO}): 2127w, 2079s, 2051s, 2017m cm^{-1}.

^1H n.m.r. (CD_2Cl_2, 298 K): δ 8.1 - 6.3 (m, 35H, phenyl region), 4.54 (dt, 1H, PCH_2P, J_{HH} = 14.7, J_{PH} = 11.0, $J_{P'H}$ = 12.5 Hz), 4.31 (dt, 1H, PCH_2P, J_{HH} = 14.6, $J_{PH} = J_{P'H}$ = 8.3 Hz), 2.95 (br, 2H, CH_2).

$^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): δ 14.7 (d, $J_{PP'}$ = 58.8 Hz), 3.8 (d, $J_{PP'}$ = 58.8 Hz).

$^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2, 298 K): (carbonyls not located), δ 133-129 (phenyl region), 82.2 (s, μ-CH_2^+), 35.7 (dd, PCH_2P, $J_{PC} = J_{P'C}$ = 27 Hz).

5.4. References

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